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NOTE ON THE PERMANENCE OF STANDARDS OF LENGTH[1]

By R. H. Field[2]

Abstract

A few reasons are presented for believing that the fundamental standards for the Metre and the Yard, and also the legal Dominion Standards of length, are not changing appreciably. On the other hand, measurements of a number of laboratory nickel-iron rules show progressive shortening which is still taking place, through periods up to 20 years.

Definition of a Permanent Length

The distance between two points of a bar will here be considered as permanent if, when the bar is subjected to a given set of conditions (temperature, pressure, method of support, etc.), measurements of any lengths in nature made with reference to the bar, at different times, do not result in variations which cannot be explained as due to some known property peculiar to the medium extending through the length measured, or to the method of measurement.

Permanence of the International Metre

No satisfactory evidence has been produced to throw doubt on the stability of the platinum-iridium alloy from which the international prototype metres are constructed. To ascertain whether relative changes had occurred, a special re-comparison between the International Standard itself (No. 6) and most of the copies was made in the period 1920–32 at le Bureau International des Poids et Mesures, Sèvres (5). For the 25 rules concerned, the mean difference between the two values (1890 minus 1920) was $+0.08\mu$. The maximum differences were -0.88μ and $+0.66\mu$, and 15 of the rules showed agreement between the two values to 0.2μ. Plausible explanations could be advanced for several of the larger discrepancies—known accidents to the rules, poor fiducial marks, excessive use and cleaning, etc.—and, when due allowance had been made for these, only in one or two cases was the difference greater than the conceded experimental errors.

It is interesting to observe that the re-comparisons just mentioned were made as a result of the insistence of the late Mr. Louis A. Fischer, Chief of the Metrology Division, National Bureau of Standards, Washington. In 1904

[1] *Manuscript received February 1, 1939.*

Contribution from the Division of Physics, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 810.

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Mr. Fischer took to Sèvres the legal standard of length for the United States (prototype No. 27) and a comparison with the International Bureau working standards, No. 26, and Type 3, indicated a shortening of 0.4μ from the original length of 27 (4). The subsequent investigations confirmed Mr. Fischer's suspicion that the Sèvres rules, and not the United States standard, had changed (5).

The change had not been detected previously, as both International Bureau prototypes were affected in the same way, and hence yielded consistent results in observations where they were employed as standards. The explanation given was that the necessary frequent wiping of the speculum "mouches", bearing the graduation lines, had changed the positions of the edges of these lines as seen through the comparator microscopes. Such an occurrence, however, in an institution like the Bureau, renowned for patient investigation and the search for "one more decimal place", illustrates the pitfalls which consistent results prepare even for experienced observers, and emphasizes the necessity for proper checks in absolute measurements, no matter how good the observations appear.

There still remains the possibility of a progressive change affecting all the prototypes alike, which is quite feasible owing to the common origin of the bars. Since Michelson's original determination of the wave-length of the red cadmium radiation at Sèvres in 1893, the experiment has been repeated from time to time by other observers, but no differences have been found which can be ascribed as due solely to changes in the standard metre.

Such experiments have, however, given one more instance of the difficulty in obtaining accuracy in absolute measurements. Within the last few years a carefully designed and constructed apparatus was built at the National Physical Laboratory, for determining wave-lengths in terms of metre or yard standards (8). It was designed for a precision of $1 : 4 \times 10^8$ in the verification of the end standards (étalons) in terms of wave-lengths, and hence the over-all accuracy should be limited only by the transfer of length between these end standards and the fundamental line standard. With the method adopted, a precision approaching 0.1 micron ($1 : 10^7$) should be possible for this operation.

Concurrently (2) equally precise determinations, for the metre, were in progress at the Physikalisch-Technische Reichsanstalt. Yet the values found at these two laboratories differed to the order of 0.5μ ($5 : 10^7$), and, so far as known, have not been reduced, even though careful checks were made, including the exchange of the experienced observers—the latest report available (2) indicating that the discrepancy continues. Incidentally, this result shows that metrologists should not be too hasty in displacing the platinum-iridium metre standard by a reference to light.

Permanence of the Imperial Standard Yard

The Imperial Standard Yard is a bronze bar, cast about 1845. Unfortunately thermometry was not then in such an advanced state as it was some forty-five years later when the metre prototypes were intercompared, and the

Committee responsible for replacing the Yard (1) did not refer their thermometers to the gas scale. Consequently the yard standard cannot be brought to its reference temperature of 62° F. with a certainty of two or three tenths of a degree (corresponding to practically as many whole microns in its length).

So far as relative differences are concerned, comparisons between the Imperial Standard and its copies have not shown conclusive evidence of change (7). In this connection it is interesting to observe that a duplicate of the Standard, Bronze Yard No. 16, made and compared at the same time as the Standard, and which is now preserved in the Museum of the National Research Council at Ottawa, was reverified at Ottawa in 1927. Its length was then found to be within 0.00008 inch from that given in reference 1 (3).

There is some evidence (7) that a similar bronze bar made in 1878 changed measurably during the first 10 years of its "life", but a comparison between the International Metre and the Imperial Yard made in 1893 yielded values differing only by 0.8μ from results obtained within the last few years (5).

Canadian Legal Standards of Length

The Canadian Legal Standard Yard is a bronze bar, one inch square in section and provided with two wells, drilled to the neutral surface, where the fiducial lines are ruled on gold plugs. It is similar to the Imperial standard. A reverification carried out at Ottawa in 1927 (3) indicated no change exceeding 0.00007 inch from the original value, obtained in London in 1874 (the reference standard being the Imperial Yard).

For the metre the Canadian standard is a nickel bar of H-section, with graduations on the exposed neutral surface. The lines on this bar (made in 1920) are considerably finer than those on any of the bronze bars previously mentioned, and consequently its length can be determined with greater precision.

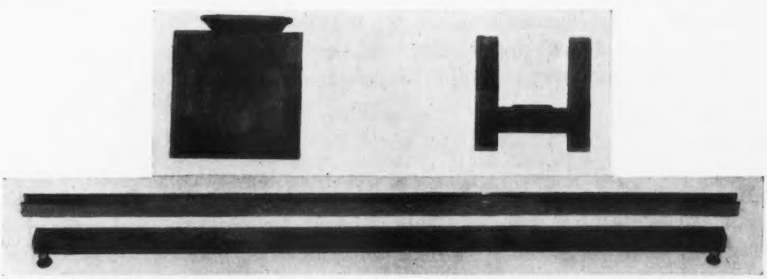

FIG. 1. *The Dominion Standard Metre (centre and right). The Dominion Standard Yard (bottom and left).*

Both legal standards are preserved in the National Research Laboratories, Ottawa, and are illustrated in Fig. 1. The upper, end photographs are

reproduced to a larger scale than the lower view, but serve to show the cross sections of the two bars.

The nickel metre rule has been compared at various times directly with platinum-iridium prototypes of the International Metre, and the results are given in Table I.

TABLE I

COMPARISON OF THE NICKEL METRE RULE WITH PLATINUM-IRIDIUM PROTOTYPES

Year	Place	Prototype No.	Length of Nickel Standard Metre (at 0° C.)
1921	Sèvres	26	1 metre + 17.0* μ
1924	Sèvres	26	+ 17.5
1928	Washington	27	+ 17.3
1929	Sèvres	26	+ 16.8

* *Corrected for the change subsequently found in the length of No. 26 (mentioned previously).*

There is no evidence in these figures of any change in the Canadian Standard Metre relative to the prototypes during the period covered, and the standard is assumed to have a length of 1 metre + 17.1μ, for determining the lengths of laboratory working standards.

Experience with Some Nickel-iron Length Standards

In the National Research Laboratories, Ottawa, five nickel-iron alloy rules are in use as secondary standards in metrological activities. These all bear fine reference lines, their thermal dilation equations are accurately known, and they can be compared with one another or with suitable standards to a precision of 0.2μ, as judged by the results obtained by different observers and in different verifications. Four of the rules are of H-section, similar to the Dominion nickel standard metre, while the fifth (No. 191) is of approximately an inverted T-section, having been made for a special purpose, but it is capable of the same precision in comparisons as the other four.

An intercomparison of these rules and the nickel standard was made in December, 1938, and yields interesting information on the stability of the former, when considered together with the results of previous verifications. Fig. 2 shows the lengths of the secondary standards plotted against a time base. These rules are ordinarily kept at room temperature, and are rarely disturbed in their individual storage cases; consequently, it would appear that the changes in length shown are due to some internal process going on in the metal, rather than to the effect of external influence.

Rule No. 191 is the oldest of the series, and was first verified in 1919. It is of 36% nickel (invar) and expands about 2 parts in 10^6 per 1° C. Despite the 20 year period of observation the curve reveals little evidence that the rule

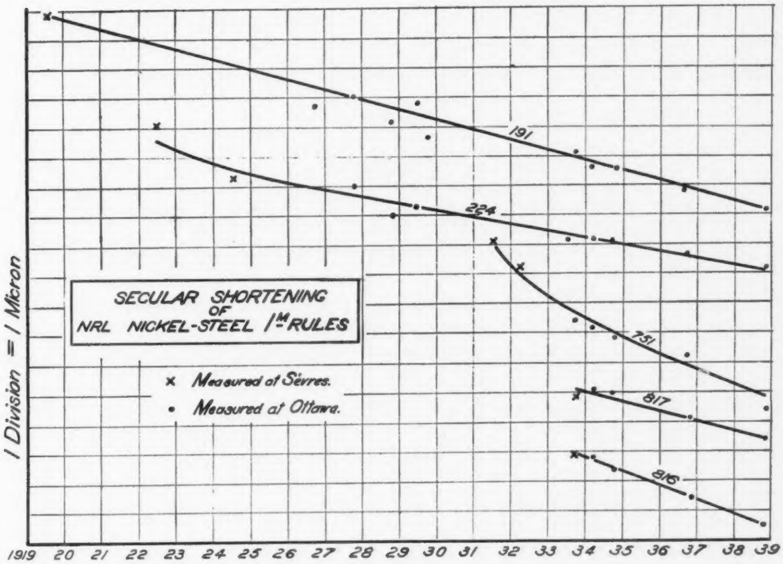

FIG. 2.

is approaching a steady length. No. 224 contains 42% nickel and has about the same thermal dilation as platinum. It, too, seems to be changing at a constant rate, even after 16 years of observation. No. 751 is a 36% nickel rule, made from the alloy known as "Fixinvar", developed by Guillaume in efforts to obtain a more stable form of the famous invar, which was known to suffer from secular change, as well as from other irreversible effects to the length. So far the results with this rule throw doubt on the accomplishments, as it has changed by 6.5μ in seven years—more than $6 : 10^6$. The thermal expansion of 751 is about 1 part in 10^6 per 1° C. Rules 816 and 817 are of 42% nickel, and also show an unmistakable shortening with time. While the evidence will not be conclusive until more comparisons have been made, the curves indicate a different rate of change for these two rules, although they were made together from the same melt.

It is understood that all these rules, purchased from La Société Genevoise d'Instruments de Physique, were submitted to the best-known methods of heat treatment to achieve stability. An interesting observation is that all the nickel-iron rules under discussion shorten with time, whereas published results of observations on invar show it to lengthen. Johnson (6) gives an instance of an invar rule at the National Physical Laboratory which lengthened by 21μ in 19 years, while Dr. Judson, Chief of the Length Section, National Bureau of Standards, informs the writer that an invar bar purchased

in 1903 is still increasing in length, being 0.75μ longer in 1938 than in 1936. It is to be noticed that tempered steel shows anomalous behaviour of the same kind. Tempered steel gauges of the Johansson type hence require periodical checking when used as standards in precise length measurements.

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UNE ÉLECTRODE ARGENT–CARBONATE D'ARGENT OBTENUE PAR ÉLECTROLYSE[1]

PAR PIERRE DEMERS[2]

Sommaire

Par l'électrolyse, avec une anode d'argent, d'une solution diluée de bicarbonate de soude, on a obtenu un dépôt adhérent de carbonate d'argent. L'électrode ainsi obtenue, immergée dans une solution de carbonate et de bicarbonate alcalin, prend un potentiel défini, reproductible, et égal à celui de l'électrode Ag (cristallin), Ag_2CO_3 (cristallin). À 25° C., le potentiel normal a été trouvé égal à -0.4769 volt, et le produit de solubilité égal à $10^{-11}\,1.27$.

Quelques auteurs ont étudié l'électrode Ag–Ag_2CO_3. Spencer et Le Pla (14), Abegg et Cox (1), et Masaki (11) se sont servis d'un bâton d'argent entouré de carbonate d'argent précipité par double décomposition. Walker, Bray et Johnston (15) ont employé de l'argent cristallin obtenu par électrolyse, et du carbonate lentement précipité par un courant de dioxyde de carbone. Les International Critical Tables (6) donnent pour valeur du potentiel normal: $E_0 = -0.50$ volt.

On connaît d'ailleurs l'importance du procédé habituellement employé par Harned (électrodes du type II) (3), qui consiste à déposer le sel d'argent voulu, par l'électrolyse d'une solution appropriée, sur une anode d'argent réduit. Moyennant quelques modifications, nous avons finalement réussi à préparer des électrodes Ag–Ag_2CO_3 selon ce principe.

I. Préparation de l'électrode

On soude bout à bout un fil d'argent à un fil de cuivre; on introduit ce fil dans un tube de verre de telle longueur que le fil en émerge aux deux bouts. On fond une extrémité de ce tube autour du fil d'argent. Avec le bout du fil d'argent qui dépasse on forme une spirale qu'on recouvre d'une pâte d'oxyde d'argent purifié, puis on réduit cet oxyde en chauffant à 450–550° C., selon le procédé usuel (7). Après refroidissement, on assure l'étanchéité du joint verre-argent, en fondant avec précaution un peu de paraffine à l'intérieur du tube. Avec cette électrode pour anode, et un fil de platine pour cathode, on fait passer 10 milliampères par cm^3 d'électrode pendant 30 min., à travers une solution $0.02M$ de bicarbonate de soude. Il se dépose sur l'argent du carbonate d'argent jaune, qui verdit facilement à la lumière.

Plusieurs électrodes préparées de cette façon, et immergées dans une solution contenant du bicarbonate de soude et du carbonate de soude, s'accordent entre elles à un ou deux dixièmes de millivolt. Des électrodes vieilles de quelques jours s'accordent moins bien entre elles, et ont été trouvées plus négatives en moyenne que des électrodes fraîches.

[1] *Manuscrit reçu le 11 octobre, 1938.*
Contribution du laboratoire de Physique de l'Université de Montréal, Montréal, Québec, Canada.

[2] *Chargé de cours, département de physique, faculté des sciences, Université de Montréal, Montréal, Québec, Canada.*

Des électrodes préparées de la façon décrite ont été comparées dans une même solution de carbonates, avec l'électrode Pt, Ag (cristallin), Ag_2CO_3 (cristallin); elles s'accordent avec cette dernière à un ou deux dixièmes de millivolt. L'argent cristallin employé pour cette comparaison, a été obtenu par l'électrolyse d'une solution chaude d'azotate d'argent, sous une forte densité de courant, selon le procédé de Lewis (7), Linhart (8), et Randall et Young (13). Le carbonate d'argent cristallin a été préparé par lent barbotage d'un courant de dioxyde de carbone dans une dissolution d'azotate d'argent ammoniacal, selon Walker, Bray et Johnston (15).

La préparation du carbonate d'argent, par dépôt électrolytique ou par réaction du dioxyde de carbone, a été effectuée à la chambre noire. La comparaison des électrodes a été opérée dans des récipients noircis.

II. Détermination du potentiel normal

Nous avons mesuré la f.e.m. E, à 25° C., de la pile suivante:

$$-\text{Ag, AgCl} \left| \text{Na}_2\text{CO}_3\ m_1,\ \text{NaHCO}_3\ m_2,\ \text{NaCl}\ m_3 \right\|$$
(compartiment et solution No. 1)

$$\text{Na}_2\text{CO}_3\ m_1,\ \text{NaHCO}_3\ m_2 \left| \text{Ag}_2\text{CO}_3(\text{électr.}),\ \text{Ag(réd.)}+ \right.$$
(compartiment et solution No. 2)

m_1, m_2, m_3, représentent les concentrations en molécules grammes par 1000 g. d'eau.

Les électrodes Ag, Ag_2CO_3 ont été préparées par le procédé décrit dans la première partie, et employées moins de 24 h. après leur traitement électrolytique; chacune n'a servi que dans une pile. Les électrodes Ag, AgCl sont du type II décrit par Harned (3). Avant de constituer la pile, nous avons lavé les électrodes pendant une heure au moins avec la solution de leur compartiment respectif. Au cours de cette opération, la solution où elles étaient immergées a été renouvelée de quatre à huit fois. Les électrodes ont été fixées dans des bouchons de liège paraffiné.

Les solutions ont été établies par pesée des produits purs et secs; les pesées ont été ramenées au vide.

Le récipient utilisé pour constituer la pile, en verre ordinaire, est divisé en deux compartiments: l'un renferme la solution 1 et l'électrode Ag, AgCl; l'autre qui est noirci extérieurement, contient la solution 2 et l'électrode Ag, Ag_2CO_3. Les compartiments sont reliés à un robinet à trois voies qui permet de les rincer et de les remplir avec la solution qu'ils doivent contenir. Ce robinet empêche le mélange des deux solutions; il n'établit la jonction entre les compartiments qu'au moment des mesures. La solution 2, plus légère, est alors au-dessus de la solution 1, ce qui empêche leur mélange par convection.

Les opérations nécessaires au lavage de l'électrode Ag, Ag_2CO_3, ainsi qu'à sa mise en place dans la pile, ont été effectuées dans une chambre noire.

Le thermostat, à eau, était réglé à 25° C. ± 0.02.

Nous nous sommes servis d'un potentiomètre de type K.

La f.e.m. atteint une valeur stable après une demi-heure, et commence à dériver après une heure et demie ou deux heures.

Nous avons tenu compte de l'hydrolyse de l'ion $CO_3^=$, selon les équations:

(1) $$CO_3^= + H_2O \rightleftarrows HCO_3^- + OH^-$$

(2) $$\frac{x(m_2 + x)}{m_1 - x} = K_{hydr} = \frac{K_w}{K_2}$$

x est la quantité hydrolysée, dont il faut augmenter la concentration du bicarbonate, et diminuer celle du carbonate. Pour K_{hydr}, négligeant sa variation avec la force ionique, nous avons adopté la valeur constante 0.000177, tirée des valeurs de K_2, la seconde constante d'ionisation de l'acide carbonique, de MacInnes et Belcher (10), et de K_w, la constante d'ionisation de l'eau, de Harned et Hamer (5). Nous avons négligé la solubilité du carbonate d'argent.

Nos résultats expérimentaux sont représentés dans le tableau 1 et sur la figure 1.

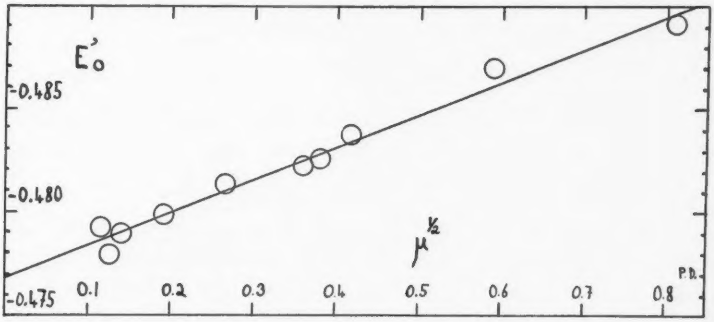

FIG. 1. *E_0' est donné par l'équation (5); μ est la force ionique des solutions No. 2: $\mu = 3m_1 + m_2 - x$. Les résultats expérimentaux sont représentés par des cercles. La droite représente l'équation appliquée selon la règle des moindres carrés: $E_0' = E_0 + b\mu^{1/2}$; pour $\mu = 0$, $E_0' = -0.4769$ volt $= E_0$, le potentiel normal de l'électrode $Ag-Ag_2CO_3$.*

Si l'on néglige le potentiel de jonction entre les solutions peu différentes, 1 et 2, la f.e.m. E peut s'écrire:

(3) $$E = E_{0\,AgCl} - E_{0\,Ag_2CO_3} - \frac{RT}{2kF} \log \frac{(CO_3^=)}{(Cl^-)^2}$$

d'où l'on tire:

(4) $$E_{0\,Ag_2CO_3} + \frac{RT}{2kF} \log \frac{y_{CO_3^=}}{y_{Cl^-}^2} =$$

$$E_{0\,AgCl} - E - \frac{RT}{2kF} \left(\log [CO_3^=] - 2 \log [Cl^-] \right)$$

$E_{0\,AgCl}$ est le potentiel normal de l'électrode Ag, AgCl, qui est égal à -0.22239 volt selon Harned et Ehlers (4); $E_{0\,Ag_2CO_3}$ est le potentiel normal cherché. Toutes les quantités du membre de droite de l'équation (4) sont connues pour une expérience donnée.

En remplaçant le membre de gauche de (4) par E_0', et en introduisant la valeur numérique du facteur $\frac{RT}{2kF}$, il vient:

$$(5) \qquad E_0' = -0.22239 - E - 0.02957 \left(\log (m_1 - x) - 2 \log m_3\right)$$

Mais l'on peut écrire:

$$(6) \qquad E_0' = E_{0\,Ag_2CO_3} + 0.02957 \left(\log y_{CO_3^=} - 2 \log y_{Cl^-}\right)$$

E_0' tend donc vers $E_{0\,Ag_2CO_3}$ à mesure que décroît la force ionique μ: puisque, selon la théorie de Debye et Hückel (2), le dernier terme du membre de droite de (6) est proportionnel à $\mu^{1/2}$, aux faibles concentrations. Il paraît légitime, au degré d'approximation de nos résultats, d'extrapoler E_0' par une fonction linéaire de $\mu^{1/2}$:

$$(7) \qquad E_0' = E_{0\,Ag_2CO_3} + b\mu^{1/2}$$

Par la méthode des moindres carrés, l'on trouve:

$$(8) \qquad E_{0\,Ag_2CO_3} = -0.4769 \text{ volt}$$

$$(9) \qquad b = -0.01575$$

La loi de Debye et Hückel prévoit pour b une valeur absolue plus élevée, $b = -0.0299$; on peut déduire de (9) que les coefficients d'activité de l'ion $CO_3^=$ sont notablement plus élevés que ne l'indique la loi limite de la théorie. Voir à ce sujet les conclusions de Lortie et Demers (9).

Du potentiel normal, on peut déduire le produit de solubilité thermodynamique du carbonate d'argent; pour une solution saturée de ce sel:

$$(10) \qquad K_{sol} = (CO_3^=)(Ag^+)^2$$

On obtient K_{sol} au moyen de l'équation suivante:

$$(11) \qquad \log K_{sol} = \frac{1}{0.02957} \left(E_{0\,Ag} - E_{0\,Ag_2CO_3}\right)$$

$E_{0\,Ag}$ est le potentiel normal de l'électrode d'argent, que nous prenons égal à -0.7991 volt selon Owen et Brinkley (12).

$$(12) \qquad K_{sol} = 1.27 \times 10^{-11}$$

Remerciements

Nous désirons remercier bien vivement l'Ecole polytechnique de Montréal qui a eu l'amabilité de nous prêter un potentiomètre de type K, dont nous nous sommes servis pour faire ces mesures.

TABLEAU I

m_1	m_2	m_3	x	μ	$\mu^{1/2}$	E	E'_0	Nombre de piles
0.1883	0.09490	0.03463	0.000345	0.6595	0.8121	0.20174	0.48914	5
0.08788	0.08687	0.01412	0.000178	0.3503	0.5919	0.18644	0.48700	3
0.04350	0.045302	0.00608	0.000169	0.1756	0.4190	0.17077	0.48381	6
0.03417	0.04368	0.01712	0.000138	0.1461	0.3822	0.19926	0.48261	3
0.03274	0.03177	0.02089	0.00020	0.1298	0.3603	0.20460	0.48226	3
0.01824	0.01596	0.003242	0.00020	0.07066	0.2658	0.16325	0.48142	3
0.008906	0.01034	0.004001	0.00015	0.03687	0.1920	0.17656	0.47992	3
0.005008	0.004676	0.001057	0.00018	0.01952	0.1398	0.14909	0.47900	3
0.003921	0.004554	0.002127	0.00014	0.01617	0.1772	0.16920	0.47799	3
0.003233	0.003755	0.001612	0.00014	0.01331	0.1154	0.16607	0.47931	3

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THE β- AND γ-RAYS OF ACTINIUM B AND ACTINIUM C″[1]

By B. W. Sargent[2]

Abstract

The absorption method of finding the end-point of a β-ray spectrum has been made more precise and free of errors that are due to straggling and the γ-ray background. The absorption curves of the β-rays of radium E and uranium X_2 were taken as standard, since, from experiments with the magnetic spectrograph, their end-points are known to be 1.15 and 2.32 Mev respectively. The extrapolated ranges of these fastest β-rays are, from experiments with homogeneous beams, 0.51 and 1.12 gm. per cm.^{2} of aluminium. In general the extrapolated range R can be expressed in terms of the energy E in Mev by the equation:

$$R = 0.526\,E - 0.094,$$

for $E > 0.6$ Mev. It is shown that the final portions of the absorption curves of the β-rays from radium E and uranium X_2 have the same shape when plotted against m/R, where m is the mass in gm. per cm.^{2} of absorber and R is the range of the fastest β-rays in the spectrum. The range and end-point of another β-spectrum can be found by fitting its absorption curve to the standard one.

The absorption curve of the β-rays of actinium B was obtained separately from that of actinium C″ for the first time. Growth curves were plotted from measurements of the β-activity of the active deposit obtained by exposing aluminium foils to filtered actinon for a few minutes. The β-activity was measured through thickness of aluminium up to 0.32 gm. per cm.^{2} From the initial portions of the growth curves and from the absorption curve of the β-rays of actinium (B + C) in equilibrium, separate absorption curves were plotted which indicated ranges of 0.64 and 0.68 gm. per cm.^{2} of aluminium for the β-rays of actinium B and actinium C″ respectively. The corresponding end-points are 1.39 and 1.47 Mev.

There is some evidence that the β-spectrum of actinium B consists of two primary components, namely, a strong one having an end-point at 1.39 Mev and a weak one having an end-point at about 0.5 Mev. The difference between the two end-points is approximately equal to the energy (0.83 Mev) of a γ-ray emitted in the transformation actinium B.C. The ratio of the numbers of β-particles in the two partial spectra is approximately 1:7. This gives an excitation probability of 0.12 for the 0.83 Mev level of the actinium C nucleus, which is of the same order of magnitude as that obtained from the intensities of the γ-rays.

Introduction

In 1908 Hahn and Meitner (21) obtained absorption curves for the β-rays of actinium C″ and of actinium (B + C) in equilibrium under the same experimental conditions. After the rays had passed through a certain small thickness of absorber, both curves of the logarithm of the ionization of the β-rays against thickness of aluminium were found to have identical slopes. The curves showed further that a weak group of easily absorbed β-rays were emitted by actinium (B + C) but not by actinium C″. Lacking further evidence, Hahn and Meitner concluded that when the source was actinium (B + C) the β-rays of actinium C″ were solely responsible for the ionization after the rays had passed through an initial small thickness of absorber, and that the easily absorbed β-rays were those of actinium B. Later, the writer (37, 38) repeated and extended the absorption measurements. In many

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careful experiments no certain difference was found in the penetrating power of the β-rays of actinium C'' and of actinium (B + C) in equilibrium after they had passed through an initial mass of 0.08 ± 0.02 gm. per cm.^{2} of paper or of aluminium. The conclusion drawn was that the β-rays of actinium B have a range of 0.08 gm. per cm.^{2} in aluminium and a maximum energy of 300,000 volts. However, there were two disturbing points. The first was that the intensity of the easily absorbed group of β-rays was too small for a complete spectrum after liberal allowance had been made for their absorption in the window of the measuring electroscope. The second point was that actinium B did not fit into either of the two groups of β-ray bodies which showed relations between their maximum energies and transformation constants (39). The energy 300,000 volts was evidently not great enough to correspond to a half-period of 36.1 min. In the light of later experimental work the following conclusion, which was not precluded by any of the absorption measurements, is more accurate. The β-spectrum of actinium B consists of a portion of low energy β-rays and a portion that is almost identical in energy distribution with the spectrum of actinium C''.

The first experimental evidence for the hard component of the β-spectrum of actinium B was obtained by Lecoin (26). Sources, which were almost pure actinium B at first, were obtained by activating strips of cellophane in actinon for a few seconds. The tracks of the β-rays emitted shortly afterwards were photographed in a cloud chamber situated in a magnetic field. A distribution curve of the β-rays was obtained from the number of tracks, their radii of curvature, and the strength of field. When corrected for a small number of β-rays from actinium C'', this shows a maximum number at an energy of 100,000, a minimum at 300,000, a maximum at 400,000, and an end-point at 950,000 volts. The energy at the minimum between the two peaks agrees well with that found by the absorption method. Supporting evidence for the high energy component was obtained by Sanielevici (36) from heating measurements with a micro-calorimeter. By assuming 470,000 volts for the average energy of the β-rays of actinium C'', he found that the average energy in the β-spectrum of actinium B was 370,000 volts. This agrees well with 360,000 volts obtained by Lecoin from the energy spectrum. Therefore, the β-rays of actinium B are much more penetrating than had been believed for 28 years.

In 1908 Hahn and Meitner (20) published some growth curves obtained from measurements of the β-activity of the active deposit collected during short exposure to actinon. However, since these had never been studied for various thicknesses of absorber, it was thought worth while to seek confirmation of the discovery of Lecoin and Sanielevici by the absorption method. Growth curves were obtained for masses of aluminium up to 0.32 gm. per cm.^{2} Separate absorption curves for the β-rays of actinium B and of actinium C'' were then deduced. The end-point of the β-spectrum of actinium C'' had been found previously to be 1.40 Mev from the range 0.62 gm. per cm.^{2}

of aluminium for the β-rays of actinium (B + C) in equilibrium (37). This end-point might be low on account of the weakness of activity and the admixture of β-rays from actinium B. Therefore, one of the main purposes of the present experiments was to establish with greater accuracy the end-points of the two spectra. By a comparison method these were found to be 1.39 and 1.47 Mev respectively for actinium B and actinium C″. If the β-spectrum of actinium B is assumed to consist mainly of two primary components, their intensities and difference in end-points are in fair agreement with the intensities and energies of accompanying γ-rays.

Experimental Details

(a) Apparatus and Adjustments

The investigation required an instrument that would measure ionization currents from 4×10^{-15} to 2×10^{-12} amp. A Compton electrometer (Cambridge Instrument Co. model) and steel ionization chambers were adopted. The electrometer was housed in a bell-jar standing on a pump plate. The connection from the insulated pair of quadrants passed downwards through the pump plate into a hollow brass block where it was joined to a horizontal brass wire, which passed axially through the two steel chambers. The first chamber was cylindrical, 12.3 cm. long and of 4 cm. inside diameter, and was fitted with brass flanges at its ends. One flange was bolted to the brass block with an insulating rubber gasket between them. The other flange was bolted to the steel end of the large steel chamber with an earthed guard-ring and rubber gaskets between the chambers. The more important insulators for the axial wire were ebonite coated with paraffin wax, as described by Bradfield (4). The large chamber was cylindrical, 15.5 cm. deep and of 13 cm. inside diameter. The β- and γ-radiations entered through a cellophane window of 0.0069 gm. per cm.^{2} in the end of the chamber. Inside the large chamber the axial electrode could be connected to earth by contact with a brass wire that could be swung through a small angle by means of its attachment to a plunger inside a small steel-clad solenoid.

The ionization chamber was maintained at a potential of 270 volts above earth with dry batteries. An atmosphere of dry carbon dioxide was maintained in this chamber by its slow continuous flow from a commercial cylinder.

The small steel chamber was originally intended to be used to balance out large γ-intensities in the large chamber. Therefore the former was made gas-tight and insulated electrically. A small mica-covered slot in its under side was provided to admit β-radiation from an old emanation tube. Alternatively this chamber might be used as the compensating condenser in the Townsend balance method. In the experiments to be described here it contained air and was earthed.

The movable quadrant and the needle of the electrometer could be raised or lowered with the aid of brass tubes inserted through the hole in the top of the bell-jar. Ordinarily, two wires from the batteries passed through

the rubber stopper in this hole to the needle and case of the electrometer. The pressure in the bell-jar was kept below 2 mm. of mercury. The electrometer was used under negative electrostatic control. With positive voltages of 24, 48, and 72 on the needle, the voltage sensitivities were 1010, 2650, and 7850 mm. per volt respectively at a scale distance of 110 cm. The corresponding current sensitivities were in the ratios 100 : 170 : 200. In these experiments the needle was maintained at 48 volts above earth, which gave a satisfactory current sensitivity and a stable zero. The capacity of the electrometer and steel chambers was 32 $\mu\mu$f. Under these conditions the natural leak of the ionization chamber of 2060 cc. volume was a drift of 2 cm. per min., or 4×10^{-15} amp. Of this the cosmic-ray intensity would be about 1×10^{-15} amp. In what follows, the β- and γ-ray intensities are expressed in centimetres per minute at a scale distance of 110 cm. from the electrometer mirror. These can be converted to amperes by multiplying by 2.0×10^{-15}.

(b) Corrections to Rates of Deflection

The rate of deflection of the electrometer needle is an oscillatory function of the time measured from the instant that the ion-collecting electrode is

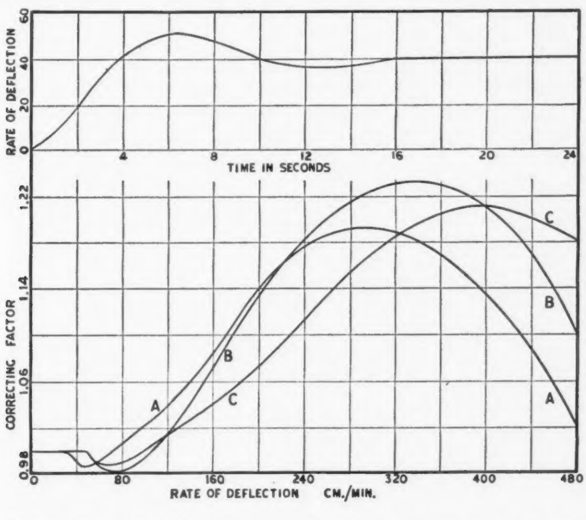

FIG. 1. *Upper graph: variation of the rate of deflection in centimetres per minute of the electrometer needle with the time. Lower graph: correcting factors for various observed rates of deflection of the needle.*

A. $\theta_0 = 7$ *cm.,* $\theta_1 = 30$ *cm.*
B. $\theta_0 = 10$ *cm.,* $\theta_1 = 30$ *cm.*
C. $\theta_0 = 10$ *cm.,* $\theta_1 = 40$ *cm.*

disconnected from earth. A graph of this function is shown in the upper part of Fig. 1. The ordinates are approximations to the instantaneous rates,

and were obtained by timing the spot of light reflected from the mirror over short distances along the scale. In measuring β- and γ-ray ionization currents it is usually impracticable to measure directly the steady rates of deflection after about 16 sec. (Fig. 1), when oscillations have practically ceased. Therefore, corrections were calculated, which, when applied to the observed rates of deflection, gave the steady rates. The latter are of course comparable measures of the β- and γ-ray intensities.

In practice, the spot of light is allowed to move from rest over a constant distance θ_0 on the scale and is then timed with a stop-watch over another constant distance $\theta_1 - \theta_0$. Let t_0 and t_1 be the times (seconds) required by the spot of light to reach θ_0 and θ_1 respectively from rest. Let $\dot{\theta}_s$ and $\dot{\theta}$ be the respective rates of drift at any chosen time t for the standard case shown in the upper part of Fig. 1 and for the general case, and $\dot{\theta}_{ms}$ and $\dot{\theta}_m$ the corresponding steady rates of drift. It was found experimentally that the shape of the curve for $\dot{\theta}$ as a function of t does not depend on the rate of deflection. A factor k can therefore be introduced to take account of the different rates; hence,

$$\dot{\theta} = k\dot{\theta}_s \quad \text{and} \quad \dot{\theta}_m = k\dot{\theta}_{ms}\,.$$

For the two observable (but different) average rates the following relations may be written:

$$\bar{\dot{\theta}} \text{ (if observed)} = \frac{\theta_0}{t_0} = \frac{k}{t_0}\int_o^{t_0} \dot{\theta}_s dt\,, \tag{1}$$

$$\text{and } \bar{\dot{\theta}} \text{ (observed)} = \frac{\theta_1 - \theta_0}{t_1 - t_0} = \frac{k}{t_1 - t_0}\int_{t_0}^{t_1} \dot{\theta}_s dt. \tag{2}$$

From these equations

$$\frac{\theta_1}{k} = \int_o^{t_1} \dot{\theta}_s dt\,. \tag{3}$$

The integral $\int_o^t \dot{\theta}_s dt$ was calculated graphically from Fig. 1, and its value plotted against its upper limit t. From this graph t_0 and t_1 were read for values of θ_0/k and θ_1/k, that is, for chosen values of θ_0 and θ_1 and for various values of k, such as 1.0, 1.5, 2.0, ... 12. If the units of rate of drift are now changed from centimetres per second to centimetres per minute,

$$\bar{\dot{\theta}} \text{ (observed)} = \frac{\theta_1 - \theta_0}{t_1 - t_0} \cdot 60 \quad \text{and } \dot{\theta}_m = k(40).$$

The required correcting factor is

$$\bar{\dot{\theta}} \text{ (observed)} \div \dot{\theta}_m \text{ or } \frac{\theta_1 - \theta_0}{t_1 - t_0} \cdot \frac{60}{k(40)}\,.$$

The calculated correcting factors plotted against observed rates of deflection are shown as Curves A, B, and C in Fig. 1. For rates smaller than 30 cm. per min. the factor is one, since the steady rates of deflection have

been attained before time measurements were begun. This point was verified by measuring the intensities of the β-rays from two radium (D + E) sources separately and together. For rates smaller than 30 cm. per min. the sum of the rates of deflection for the two sources measured separately was always equal within $\frac{1}{2}\%$ to the rate for the two sources together. Further, after the corrections shown in Fig. 1 were applied, all decay graphs of actinium B or of actinium C'' plotted semilogarithmically were found to be straight lines with the same slope.

Range Method of Determining Maximum Energies of β-Spectra

Early absorption measurements by Schmidt (40, 41, 42) and Gray (16) showed clearly that the β-rays of radium E and of actinium (B + C) have definite ranges. These could have been compared with the extrapolated ranges of homogeneous β-rays, first measured by Wilson (48) in 1909, with the purpose of finding the maximum energies or end-points of these spectra. However, the absorption method was not generally applied until a program was started in the Cavendish Laboratory in 1927 for finding the maximum energies of the β-particles from many substances. The results of these experiments were presented in papers by Chalmers (5), the writer (37, 38, 39), and Feather (11).

Recent progress on the theoretical explanation of the β-spectrum and on the interrelation of partial β-spectra and γ-rays has placed emphasis on the need for more and improved measurements of end-points. While the absorption method has been widely applied to the β-emission of the new radioactive bodies, only in certain cases have the ranges and the corresponding end-points been determined with high accuracy. This is due to the lack of an exact definition of the range of a continuous spectrum. It has been known for some time that the good agreement between the end-points of certain natural β-bodies by the range method and by magnetic analysis is partly fortuitous. Two factors oppose each other near the end of the range. While the extrapolated range of homogeneous β-rays is exactly defined, it must be remembered that β-ionization is detectable well beyond this range. This effect may be called straggling. On the other hand, the limited activity of natural sources and the finite sensitivity of the measuring instrument impose a limit on the detection of the β-rays having energies just below the maximum. Further, the limit of accuracy of readings imposes a severe restriction when there is a large γ-ray background.

While the previously accepted range of the β-rays of radium E was about 0.475 gm. per cm.^{2} of aluminium, Gray and Henderson (18) found that these β-rays were detectable through aluminium of more than 0.60 gm. per cm.^{2} when a powerful preparation was placed close to an electroscope. Gray (17) suggested that the range might be defined as that thickness of aluminium which reduces the ionization of the β-rays to 1 part in 50,000 for its initial value. One should not, however, expect this definition to be applicable with

equal accuracy to other spectra of β-rays. Baschwitz (2, 3) has recently studied the effect of strength of source, γ-ray background, solid angle subtended at the source by the ionization chamber or counter, and canalization of the beam of β-rays, on their range found in a special way. The main factor that modified the value obtained for the range seems to be the γ-ray background. This is shown in a striking manner in the case of thorium C$''$, which emits a large amount of γ-radiation. The observed range is 0.47, while the expected range is about 0.85 gm. per cm.^{2} of aluminium from the known end-point of this β-spectrum. After studying the effect of experimental conditions on the range, Widdowson and Champion (47) developed an objective method of treating absorption data based on the absorption of the β-rays of radium E and thorium C. While the present paper was being written, a paper by Feather (13) appeared which describes a method very similar to that to be outlined here.

The writer has adopted a comparison method of finding the ranges of continuous β-spectra in order to avoid errors due to unequal straggling and unequal γ-ray backgrounds for different bodies. The β-rays of radium E and uranium X_2 were chosen as standards*, since their maximum energies have been determined with precision in magnetic spectrographs. The end-point of radium E has recently been determined by several experimenters (1, 14, 25, 29, 32, 46) with concordant results. A value for $H\rho$ of 5280 gauss-cm. or 1.15 Mev is chosen. The end-point of uranium X_2 is 9300 gauss-cm. or 2.32 Mev, according to Ward and Gray (46). Further, it is necessary to know the corresponding ranges for these and other energies. The best values of the extrapolated ranges of homogeneous β-rays, measured by Varder (45), Madgwick (30), and Marshall and Ward (31), are simply represented above 0.6 Mev by the linear equation:

$$R = 0.526\,E - 0.094, \tag{4}$$

where R is the range in grams per square centimetre of aluminium for β-rays of energy E expressed in Mev.† (For the ranges at lower energies the graphs given by Marshall and Ward (31) should be consulted.)

Some of the absorption measurements, plotted semilogarithmically, are shown in Fig. 2. The sources were thin and covered an area of 3 or 4 sq. cm. of glass or of aluminium, which reflect the β-rays equally. These were placed 8 cm. from the cellophane window of 13 cm. diameter in the ionization chamber, and the aluminium absorption sheets were placed close to the window. It was necessary to use two preparations of radium (D + E) of

* *The first use of these bodies for comparison was probably that of J. A. Gray and W. J. Henderson (22) in their study of the β-rays of potassium about three years ago.*

† *The linear equation* R = aE + b *connecting the range* R *of a* continuous *spectrum and the maximum energy* E *has been frequently used since it was proposed by Feather (11) in 1930. From time to time new values of the constants* a *and* b *have been proposed (47, 13).*

In calculating the constants in Equation 4, great weight was given to the results of Marshall and Ward. On the suggestion of Dr. J. A. Gray a correction of +1.2% was applied to their values of the magnetic field below 500 gauss. Energies were calculated using $e/m = 1.7575 \times 10^7$ *e.m.u. per gm.,* $e = 1.601 \times 10^{-20}$ *e.m.u. and* $c = 2.9978 \times 10^{10}$ *cm. per sec.*

quite different activities to obtain a complete curve. Both were covered with mica of 0.0062 gm. per cm.[2] Three preparations of uranium X were used, although the results for one only are shown in Fig. 2. In this case the

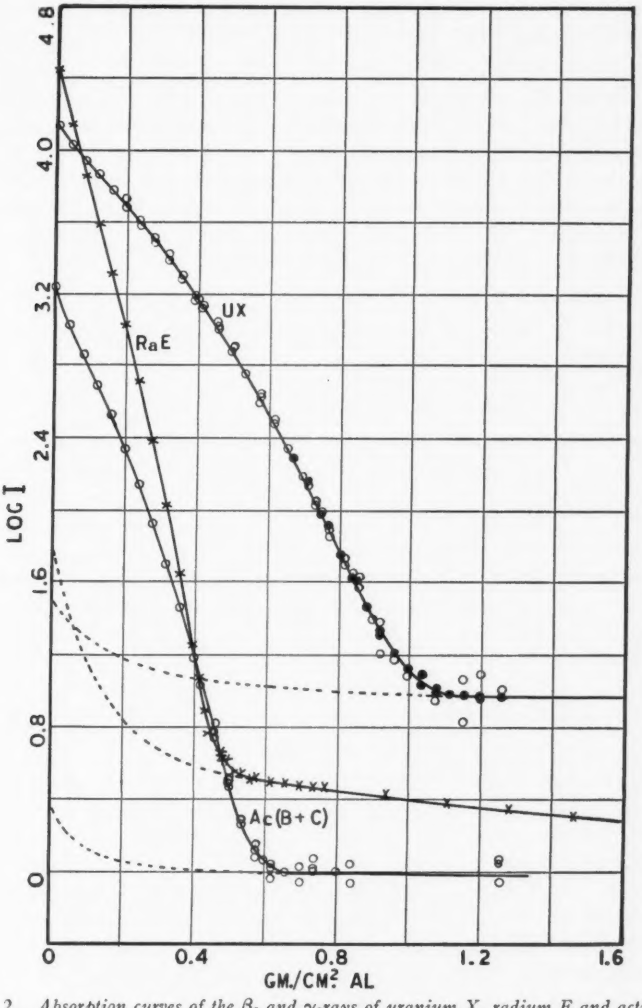

FIG. 2. *Absorption curves of the β- and γ-rays of uranium X, radium E and actinium (B + C). In order to avoid confusion the logarithms of the intensities in centimetres per minute were reduced by 0.400 in the case of radium E and by 0.300 in the case of actinium (B + C). The intensities shown are true measures of the most active source used.*

active material was placed at the end of a glass tube, 1.6 cm. in diameter and 2 cm. long. The logarithms of the intensities of the canalized beam of β-rays are indicated by filled circles when the preparation was new, and by

unfilled circles when it was from three to eight months old. By this time the activity had fallen to 6% or less of the initial value. The active deposit of actinium was obtained by recoil on aluminium discs 2 cm. in diameter. These discs were coated with shellac on one side and dried before exposure to the actinon. After activation the shellac and the undesired active deposit were removed from the one side of the disc with chloroform.

The γ-intensities for absorbers having a mass per square centimetre less than the ranges of the β-rays were estimated with the aid of curves published by Rutherford and Richardson (33, 34, 35), and are shown in Fig. 2 by the broken lines. The ranges of the β-rays of radium E, uranium X_2, and actinium (B + C), by inspection of Fig. 2, are 0.56, 1.10, and 0.64 gm. per cm.[2] respectively. When corrected for the intervening air, cellophane window, and mica these become 0.58, 1.12, and 0.67 gm. per cm.[2] Values found in

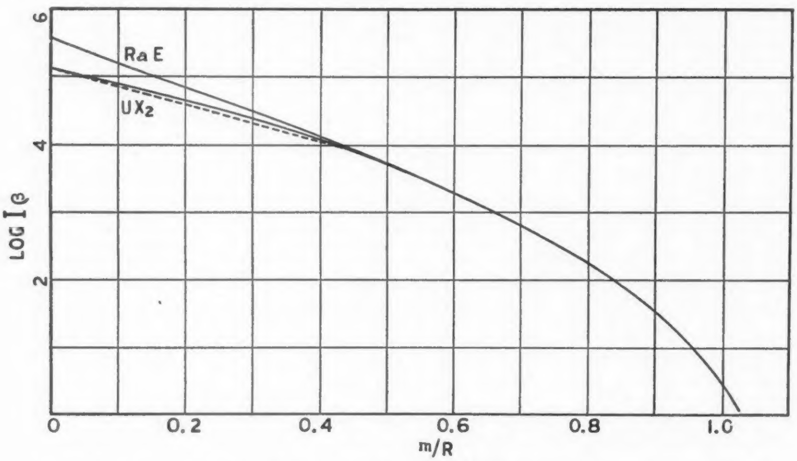

FIG. 3. *Absorption curves of the β-rays of radium E and uranium X_2. m is the mass in grams per square centimetre of absorber, and R is the extrapolated range of the fastest β-rays in the spectrum. R = 0.51 for radium E and 1.12 gm. per cm.[2] for uranium X_2.*

a similar way by others are 0.47–0.61 (3, 11, 16, 18, 40) for radium E; 0.95, 1.10, and 1.11 (3, 39, 12) for uranium X_2; and 0.62 and 0.60–0.65 (37, 3) for actinium (B + C). However, good agreement of the absorption limits determined by inspection with different experimental arrangements is not expected.

After the γ-intensities had been subtracted, the logarithms of the β-intensities were plotted against m/R (Fig. 3), where m is the mass per square centimetre of all intervening material and R is the extrapolated range corresponding to the known end-point. R was taken to be 0.51 gm. per cm.[2] for radium E and 1.12 gm. per cm.[2] for uranium X_2. It is seen that the curves for radium E and uranium X_2 are coincident between $m/R = 0.5$ and 1. This

supports the underlying assumption that many β-spectra have the same shape between the maximum energy and one-half of it.

In order to see to what extent the standard absorption curve is influenced by the angular width of the beam and by reflected β-rays, two additional preparations of uranium X were tried. One was distributed over 8 sq. cm. of a watch-glass. The β-absorption curve for this case is shown by the broken line in Fig. 3. The third preparation had an area 7 mm. $\times$ 10 mm. and was also mounted on a watch-glass. A lead plate, containing a circular hole, 1 cm. in diameter, and placed half-way between the source and the chamber window, limited the beam. The absorption curve (not shown) in this case falls more rapidly between $m/R = 0$ and 0.1, but it is coincident with the broken curve for all larger values. Therefore, after most of the reflected β-rays have been removed by absorption, the absorption curve has a definite shape, while its slope changes progressively from point to point.

The empirical rule, $R\mu/\rho = 7.5$, connecting the range R with the mass absorption coefficient μ/ρ in aluminium, given by Chalmers (6), does not hold with accuracy for these β-spectra. If $R\mu/\rho$ were a constant then the initial parts of the curves would also be coincident. However, μ/ρ is usually determined from the initial straight portion, and this is highly susceptible to the reflected β-rays from the material behind the source and to the shape of the energy spectrum in the low energy region. The absorption coefficients from the straight portions of Fig. 3 are 16.6 and 5.80 for radium E and uranium X_2, while the products $R\mu/\rho$ are 8.5 and 6.5 respectively. It does not seem likely that two values of $R\mu/\rho$, such as 6.5 and 8.5, are sufficient to represent generally the results for the two groups of permitted and forbidden transitions. In agreement with Feather (13), it is seen that there is a greater proportion of slow β-rays in the spectrum of radium E than in that of uranium X_2. At the ranges chosen here the β-ionization has been reduced to 1 part in 125,000 and 1 part in 45,000 respectively for radium E and uranium X_2.

The range of another β-spectrum can be found, accurate to 2% under the most favourable conditions, by fitting its absorption curve onto the standard curve of Fig. 3. The source must be strong enough to allow measurements of the β-radiation penetrating aluminium of mass per unit area greater than half the range. Of course the further the measurements can be carried the more accurate will be the derived range. The agreement of the new absorption curve with that of Fig. 3 above $m/R=0.5$ can be tested by trying a series of values of R. A number of equally spaced points are chosen on the new curve (log I_β plotted against m), and the values of log I_β are read. Using one of the chosen values of R, the ratios m/R are calculated for these points. The corresponding values of log I_β are then read from the standard curve and subtracted from those observed at the chosen points. This is repeated for other values of R until the differences in the logarithms become constant for various values of m/R. The value of R for this best fit is the desired range, and the corresponding energy is found from Equation 4.

When the absorption curve for the β-rays of the combined spectra of actinium (B + C) is compared with the standard curve, the best agreement is obtained with $R = 0.66$ gm. per cm.[2] At low values of m/R the curve for actinium (B + C) falls below that for radium E but above that for uranium X_2. However, the ranges of the β-rays of actinium B and actinium C″ separately can be found after the composite curve has been split up with the aid of information to be given.

Theoretical Growth Curves of Actinium Active Deposit

The active deposit of actinium was obtained by exposing an aluminium foil to decaying actinon for a few minutes. For the purpose of calculation, the supply of actinon is assumed to be constant during the activation, and in practice the supply was maintained by pumping fresh actinon into the activation chamber either continuously or at frequent intervals. Further, since the next product, actinium A, has a very short half-period, it may be assumed that its successor, actinium B, is collected on the foil at a constant rate, say one atom per second. Let P, Q, and R represent the numbers of atoms of actinium B, C, and C″ respectively at any time t measured from the end of the exposure of duration T, and λ_1, λ_2, and λ_3 their respective transformation constants. From the Rutherford-Soddy theory of successive transformations it can be shown that

$$P = 3125(1 - e^{-\lambda_1 T})e^{-\lambda_1 t},$$

$$Q = 198.9(1 - e^{-\lambda_1 T})e^{-\lambda_1 t} - 11.90(1 - e^{-\lambda_2 T})e^{-\lambda_2 t},$$

$$R = 504.8(1 - e^{-\lambda_1 T})e^{-\lambda_1 t} + 21.8(1 - e^{-\lambda_2 T})e^{-\lambda_2 t} - 114.6(1 - e^{-\lambda_3 T})e^{-\lambda_3 t}.$$

The transformation constants used were $\lambda_1 = 0.000320$, $\lambda_2 = 0.005348$, and $\lambda_3 = 0.002427$ sec.$^{-1}$. The values of λ_1 and λ_3 were verified in separate experiments.

The α-activity of the active deposit is proportional to $\lambda_2 Q$, graphs of which are shown in Fig. 4. The β-activity is proportional to $k\lambda_1 P + \lambda_3 R$ (when the β-activity of actinium C is neglected). The constant k is the relative activity of actinium B to actinium C″ and depends on (i) the average number per atom, (ii) the ionization per particle, and (iii) the penetrating ability of the β-particles of actinium B relative to those of actinium C″. Calculated curves of the variation of the β-activity of the active deposit, obtained during an exposure of four minutes, with the time measured from the end of the exposure, are shown in Figs. 5 and 6. For convenience later, these, for different values of k, were made coincident over the time range 50 to 60 min. If the values of k for different absorbers can be found experimentally then separate absorption curves can be deduced for the β-rays of actinium B and actinium C″ from the composite absorption curve for actinium (B + C) in equilibrium.

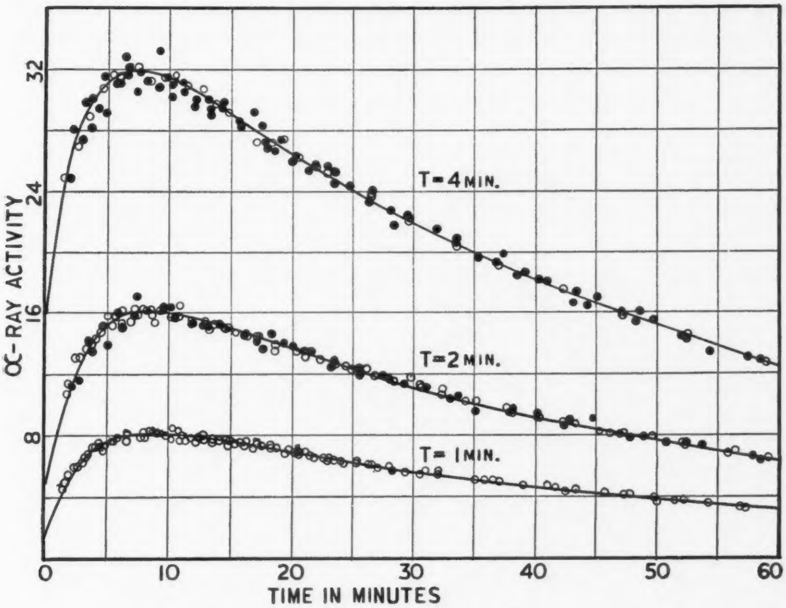

FIG. 4. *Growth curves of the α-ray activity of active deposit obtained by exposing an aluminium foil to filtered actinon for a time* T.

Experimental Growth Curves of Actinium Active Deposit

The activation chamber was a brass tube, 7.5 cm. long and 3 cm. in diameter, closed at its ends by two rubber stoppers through which passed glass tubes containing stopcocks. One was connected to the actinium container and the other to an aspirator. The aluminium foil to be activated had an area 5 cm. × 10.5 cm. and was rolled up in contact with the inner surface of the brass tube. A collecting potential difference of about 500 volts was maintained between the tube and an axial wire. Air containing actinon was drawn into the tube, usually at 15-sec. intervals.

Steps were taken to prevent any old active deposit from being carried over from the actinium container, (i) by maintaining a sweeping electric field in this container, and (ii) by the use of filtering plugs of cotton and glass wool inserted in the short connecting tube at its entrance to the activation chamber. Since old active deposit collected on the aluminium foil would change the shape of the growth curve of the β-activity at the beginning, where its accuracy is most desired, a special investigation was necessary to test the efficacy of these precautions. If any actinium C were carried over and deposited on the foil, the experimental growth curves of the α-activity would not agree with the calculated ones. Consequently α-activity-time curves were obtained with an α-ray electroscope. After small corrections were applied for the

β-activity, which varied with time in accordance with the curves in Fig. 5, the α-ray readings were multiplied by the factor that gave the best agreement with the theoretical curve between 15 and 60 min. Since the times

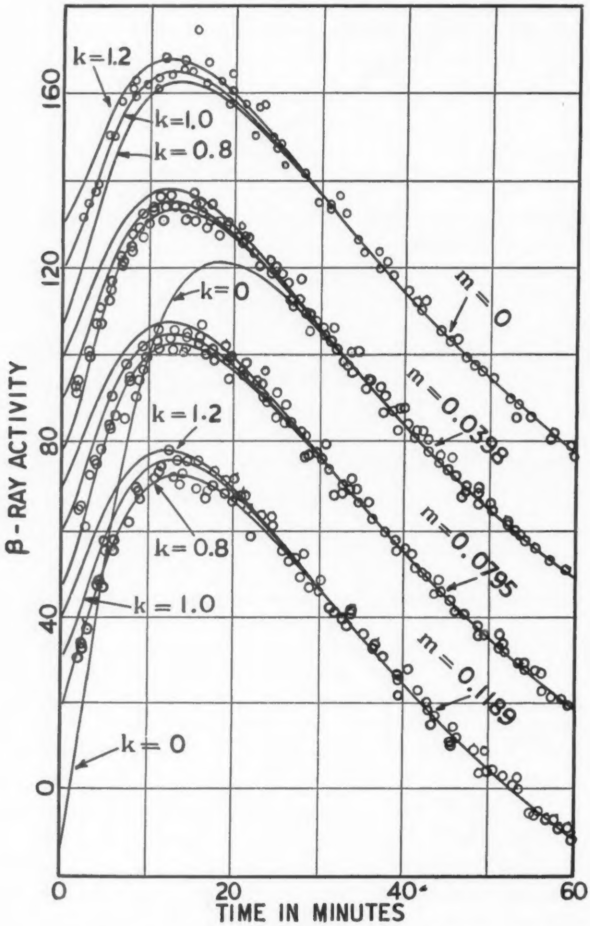

FIG. 5. *Growth curves of active deposit obtained by exposing an aluminium foil to filtered actinon for four minutes. The β-ray activity is measured through aluminium of mass* m *in grams per square centimetre. The ordinates shown apply to the uppermost set of curves* (m = *0*). *The other curves have been displaced downwards by multiples of 30 units.*

for the α-ray readings were always short, no errors were introduced when they were plotted at their mid-points of time. The results of four runs are included on each curve in Fig. 4. Points marked by filled circles refer to experiments in which the air and actinon were drawn through a bottle of water and glass

wool in addition to the usual filters. No difference was found. Since the observed values increase with time in good agreement with the calculated curves, the actinon reaching the activation chamber was free of actinium C.

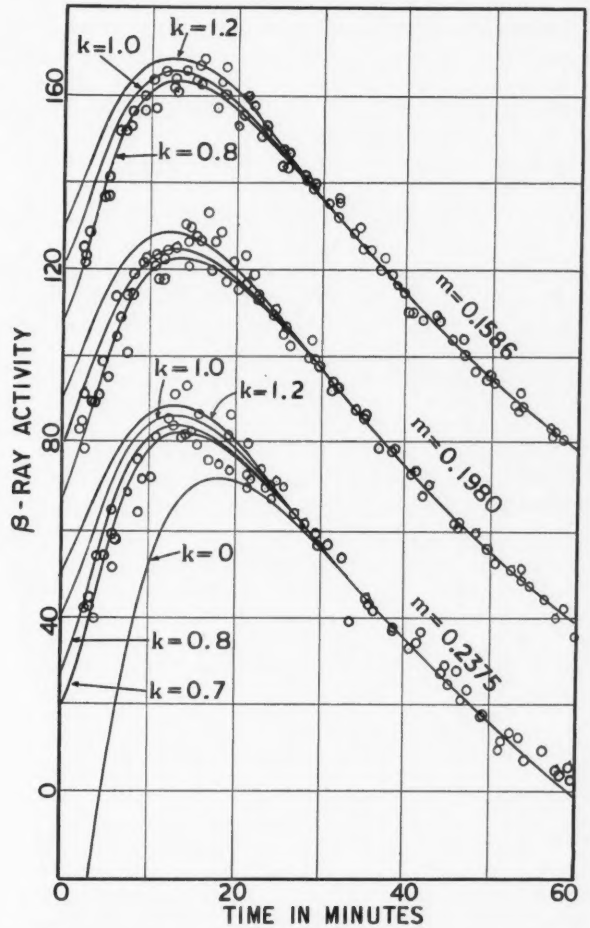

FIG. 6. *Growth curves of the active deposit obtained during a four minute exposure to filtered actinon.* m *is the mass in gm. per cm.² of aluminium absorber. The ordinates shown apply to the uppermost set of curves* (m = 0.1586). *The other curves have been displaced downwards by multiples of 40 units.*

It seems likely therefore that this actinon was also free of actinium B and actinium C″.

For a study of the β-activity, the aluminium foil of 0.0032 gm. per cm.², after its exposure to actinon, was folded over once with the active deposit

inside and mounted on a thick plate of aluminium. This was placed 2.5 cm. from the window of the ionization chamber, and the β-activity penetrating a given absorber was followed for one hour. The rates of deflection (after correction for natural leak) were multiplied by the factor that gave the best agreement with the theoretical curves in the region 20 to 60 min. Only in a few cases were the electrometer readings of sufficient duration (five minutes) that corrections were considered necessary when the rates of deflection were plotted at their mid-points of time. These corrections are the ratios of the time average of the activity over the interval $t_2 - t_1$ of the reading to the activity at the mid-point of the interval. The former is

$$\frac{1}{t_2 - t_1}\int_{t_1}^{t_2} (k\lambda_1 P + \lambda_3 R)\,dt.$$

Experimental results obtained with the electrometer are shown in Figs. 5 and 6 and in Table I. Four or five runs were taken for each mass m per unit area of aluminium and at each time T of activation. It is seen at once that, since k is nearly 1 initially and decreases slowly with m, the energy spectrum of actinium B is not quite as extensive as that of actinium C″.

TABLE I

Initial absorbers: aluminium, 0.0032; air, 0.0030; cellophane, 0.0069 gm. per cm.²

m, gm./cm.² Al	k (observed)				Limit of error	Average k
	T = 1 min.	T = 2 min.	T = 4 min.	T = 10 min.		
0	0.95	0.95	0.97	—	±0.05	0.96
0.0398	0.90	—	0.90	—	0.05	0.90
0.0795	0.85	—	0.85	—	0.05	0.85
0.1189	—	0.80	0.80	—	0.05	0.80
0.1586	—	—	0.80	—	0.05	0.80
0.1980	—	—	0.80	—	0.10	0.80
0.2375	—	—	0.72	—	0.10	0.72
0.2766	—	—	—	0.67	0.10	0.67
0.3164	—	—	—	0.65	0.15	0.65

Earlier evidence for the penetrating component of the β-spectrum of actinium B was obtained with a Geiger-Müller counter and a scale-of-two recording circuit. In this case the active deposit was collected directly on the inside of the brass cylinder forming the activation chamber. This was placed coaxially with a paper cylinder, a copper absorber, and the Dowmetal counter. The paper of 0.0057 gm. per cm.² prevented contamination of the counter and absorbers. The numbers of particles per minute were recorded. After corrections for the β-particles missed owing to the finite relaxation time of the recorder, and for the natural count, had been applied, moving averages in particles per minute were taken over six-minute intervals. The values of k for best agreement with the theoretical growth curves are shown in Table II.

TABLE II

Initial absorbers: paper, 0.0057; air, 0.0007; Dowmetal F, 0.0354 gm. per cm.²

m, gm. per cm.² Cu	k (observed)		Relative intensity Ac (B + C) in equilibrium
	T = 1 min.	T = 1.5 min.	
0	1.0 ± 0.1	1.0 ± 0.2	100
0.104	—	0.9 ± 0.1	22.7 ± 0.9
0.168	—	0.8 ± 0.2	9.87 ± 0.54

Absorption of the β-rays of Actinium B and of Actinium C''

The absorption data of Table III were obtained for the β-rays of actinium (B + C) in equilibrium, actinium C'', and radium E, when the sources were mounted on aluminium and placed 2.5 cm. from the window of the ionization chamber. The ratio k (Table I), of the ionization produced by the β-rays of actinium B to the ionization produced by those of actinium C'' at each absorber thickness, being known, the composite data of Column 2 (Table III) for actinium (B + C) were resolved into the separate groups for the β-rays of actinium B and C'' given in Columns 3 and 4. The values in Column 4 obtained in this way are in good agreement with those in Column 5 obtained directly with pure sources of actinium C''. The estimated errors given in this column (and in Column 4 of Table II) are the averages of the differences from the average values of four independent sets.

TABLE III

Initial absorbers: aluminium, 0.0032; air, 0.0030; cellophane, 0.0069 gm. per cm.² (for RaE, mica 0.0062 instead of aluminium 0.0032 gm. per cm.²)

m, gm. per cm.² Al	Relative intensity				
	Ac (B + C)	AcB	AcC''	AcC''	RaE
0	100	100	100	100	100
0.0398	64.0	61.8	66.1	66.1 ± 0.4	42.9
0.0795	41.1	38.6	43.5	44.0 ± 0.4	20.9
0.1189	26.8	24.3	29.2	29.4 ± 0.2	10.7
0.1586	17.4	15.8	19.0	18.9 ± 0.2	5.58
0.1980	10.8	9.80	11.8	12.0 ± 0.2	2.73
0.2375	6.60	5.63	7.53	7.54 ± 0.07	1.29
0.2766	3.90	3.18	4.59	4.54 ± 0.06	0.575
0.3164	2.24	1.80	2.67	2.67 ± 0.04	0.245

After allowance had been made for small amounts of γ-radiation, the absorption curves for actinium B and actinium C'' were fitted to the absorption curve for radium E (Table III), over the region investigated, by the method explained earlier. Best agreement was obtained when the ranges of the β-rays of actinium B and C'' were respectively 0.65 and 0.68 gm. per cm.²

The composite curve for actinium (B + C), placed 8 cm. from the chamber, given in Fig. 2 was next resolved into separate curves by using the same values of k for the same total mass per unit area of absorber as in Table I. Further, it was necessary to extrapolate for k beyond the limit of direct measurement (m = 0.32 gm. per cm.^{2}). The ranges obtained with the aid of the standard curve of Fig. 3 are 0.62 and 0.68 gm. per cm.^{2} Therefore, 0.64 and 0.68 gm. per cm.^{2} may finally be taken to be the respective ranges of the β-particles of actinium B and C″. The corresponding energies from Equation 4 are 1.39 and 1.47 Mev.

From the energy spectrum of actinium B obtained with a cloud chamber, Lecoin (27) has concluded that the end-point is 1.00 Mev by inspection and 1.25 Mev from a Konopinski-Uhlenbeck plot. While the extent and accuracy of the absorption measurements of the present paper were severely restricted by the small activity available, it seems reasonably certain that this upper limit of energy is greater than 1.25 Mev. This conclusion is conditional on the assumption that this β-spectrum does not descend towards its limit more sharply than the average spectrum.

Further, Lecoin (27) has obtained two end-points, namely, 1.50 and 1.85 Mev, of the β-spectrum of actinium C″ by a K−U plot. The presence of a small fraction of the β-rays having the higher limit was taken to indicate a partial spectrum. Most of the disintegrations should therefore be accompanied by a γ-ray (or γ-rays) of 0.35 Mev energy. In the next section it will be shown that the γ-rays of actinium C″, if they exist at all, are very weak.

The γ-rays of Actinium (B + C)

The absorption of the γ-rays of actinium (B + C) has been studied by Rutherford and Richardson (35), and by Curie and Savel (8). The γ-rays of actinium X and its products were found by the former to have a mass absorption coefficient of 0.073 in aluminium of thickness between 6 and 9 cm. The latter obtained 0.076 for the mass absorption coefficient in lead of thickness between 4.6 and 10.6 cm. when the source was actinium and its products. It seems likely that both coefficients refer to the more penetrating γ-rays of actinium (B + C). The energies of these were most accurately obtained by Graf (15), Surugue (43), and Choong and Surugue (7) from the energies of the internal conversion electrons and their binding energies. The more intense γ-rays are listed in Table IV.

The origin of the 0.3497 Mev γ-ray is definitely known, since its energy is equal to the difference in energy of the two groups of α-particles from actinium C. The origin in each of the remaining cases was originally based on the best numerical agreement obtained in the γ-ray energy when the binding energies of atoms of the correct atomic number were added to the energies of the conversion electrons from the different levels. The assignments to the transition actinium B.C have been verified by an experiment by Choong

and Surugue (7), in which they failed to find any strong β-ray lines from a source of pure actinium C''. In a preliminary experiment the writer found by ionization through 1 cm. of steel in a pressure chamber that the γ-rays of actinium C'' are less than one-quarter as intense as those of actinium (B + C) in equilibrium for equal β-ray activities of actinium C''.

TABLE IV

Energy, Mev	Origin	γ-Ray intensity, $p(1-\alpha)$	Nuclear excitation probability, p	γ-Ray energy per disintegration, Mev
0.4040	AcB.C	0.062	0.066	0.0250
0.4258	AcB.C	0.058	0.062	0.0247
0.8296	AcB.C	0.132	0.133	0.1095
0.3497	AcC.C''	0.144	0.160	0.0504
	Total	0.396		0.2096

The intensities of the γ-rays were estimated by Li (28) from the relative photographic intensities of the secondary β-ray lines measured by Surugue (44), the absolute intensity of the *K*-line of the 0.3497 Mev γ-ray, and the values of the internal conversion coefficients α. Since the type of nuclear transition in which a given γ-ray is produced is not known, several choices of α should be considered. Li has used the values for electric dipole and quadripole radiation taken from the empirical curves of Hulme, Mott, Oppenheimer, and Taylor (23). While the γ-ray of 0.3497 Mev energy must be electric quadripole to agree with the relative intensities of the two groups of α-particles from actinium C, the character of the other γ-rays is not definite. Differing from Li in the cases of the 0.404 and 0.425 Mev γ-rays, all have been assigned intensities in Table IV on the assumption of electric quadripole radiation. These intensities are the smaller of the two choices being considered, by a factor lying between 3 and 3.8, and therefore are in better agreement with the ionization measurements of Kara-Michailova (24) and the writer. From the ionization measurements of Curie and Savel (8) the intensity of the hard γ-ray of 0.8296 Mev was estimated at 0.079 by Kara-Michailova. Further, the total γ-ray energy per disintegration of actinium (B + C) was found (24) to be 0.107 Mev by comparison with thorium (B + C) and radium C.

The writer has made a rough determination of the ratio of the number of γ-quanta to the number of primary β-particles from the measurements of Fig. 2. The intensity of the γ-rays was measured through 0.80 gm. per cm.^{2} of aluminium, and their mass absorption coefficient in the next 6.3 gm. per cm.^{2} of aluminium was about 0.050 when the absorber was close to the chamber. When corrections for absorption were applied the initial intensities of the β- and γ-rays were respectively 4200 and 2.12 cm. per min. The intensity of the β-rays of actinium B alone was about 2100; and this must be

reduced by the factor 1.32 on account of reflection from the aluminium discs. The mass absorption coefficient of the β-rays is about 9.0 in paper. It may be assumed that 0.050 and 9.0 are the coefficients of the γ- and β-rays in the carbon dioxide filling the ionization chamber. In accordance with a method used by Gray and Hinds (19) the relative ionization currents must be divided by the respective absorption in the gas and by the average energies in order to obtain the relative numbers of β-particles and γ-quanta. The average energies of the β-particles of actinium B and of the γ-rays of actinium (B + C) are assumed to be 400,000 and 450,000 electron volts. Finally, the number of γ-quanta from actinium (B + C) is about 19 per 100 β-particles from actinium B. While this estimate may be in error by as much as 50%, it agrees with the measurements of Kara-Michailova. However both disagree with the values expected from the work of Li (28) and Surugue (44) (Table IV). While the cause of the discrepancy* is not apparent, it is perhaps worth mentioning that the γ-ray intensities of Table IV would be reduced if all or part of the γ-rays of actinium B were assumed to be magnetic dipole instead of electric quadripole radiation (23).

Partial β-Spectra and the γ-Rays of Actinium B

As mentioned in the introduction, there is some evidence both in Lecoin's energy spectrum (27) and in absorption experiments by the writer (37, 38) for a weak component and a minimum number at 300,000 volts in the β-spectrum of actinium B. The intensity of the low energy peak is of the order of magnitude of 1 in 10 for the main component. While the weak component occurs in the region of some of the β-ray lines, Li (28) has found at most 3.3 secondary β-rays per 100 disintegrations. Though the evidence for two partial spectra is admittedly weak, it is in approximate agreement with the general hypotheses of Ellis and Mott (10) and the energies and intensities of the γ-rays.

Owing to overlapping, the end-point of the soft component must be greater than the energy of 300,000 volts at the minimum in the combined energy spectrum; and, from graphical attempts at breaking up the spectrum into two reasonable components, 500,000 electron volts may be taken as its approximate value. Further, owing to overlapping, the ratio of the numbers of β-particles of the soft to hard components must be increased from 1 : 10 given above to 1 : 7, and it may be as high as 1 : 5.

The actinium B nucleus may transform into actinium C in the ground state in a number of ways, as indicated in Fig. 7. The energy levels of the excited nucleus of actinium C were taken from the paper by Choong and Surugue (7). By the less frequent mode of transformation the actinium B nucleus emits a β-particle and a neutrino of 0.50 Mev energy, and the resulting

* *If the photographic intensities of the β-ray lines, measured by Surugue, are corrected for the variation of the blackening of the plates with energy, the intensity of the 0.8296 Mev γ-ray may be increased by as much as 50% [Ellis (9)]. This would increase the discrepancy.*

excited nucleus falls to the ground state usually with the emission of one γ-ray of 0.829 Mev or two γ-rays of 0.425 + 0.404 Mev energy. By the more frequent mode of transformation the actinium B nucleus emits a β-particle and a neutrino of 1.39 Mev energy.

From the relative β-intensities given above, the excitation probability of the 0.829 Mev level is approximately 0.12, and it may be as high as 0.17.

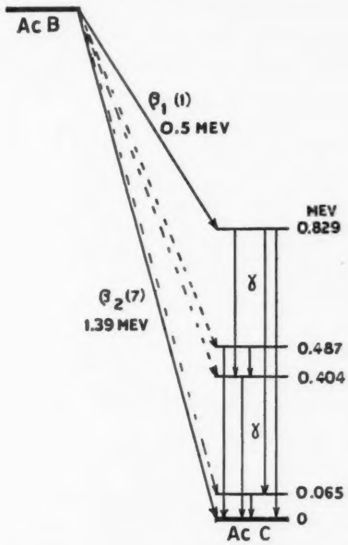

FIG. 7. *The transformation actinium B.C. The energy levels of the excited nucleus of actinium C are shown.*

From Table IV, based on Li's work, the corresponding value is 0.195. In view of the difficulties of measuring β- and γ-ray intensities the agreement is as good as can be expected.

If the tentative explanation presented here can be confirmed it provides a striking example in favour of the use of maximum energies instead of average energies of β-spectra. If the average energies of the partial spectra are assumed to be 0.15 and 0.45 Mev, the disintegration energy is 0.15 + 0.83 =0.98 Mev by one path and 0.45 Mev by the alternative path. The discrepancy is more striking than in the well known thorium C branching, where the large α-ray energies mask the disagreement.

The difficulty, mentioned in the introduction, in connection with actinium B in the log-log plot of end-points against transformation constants (39), is now partly removed. The partial transformation constants are 0.000040 and 0.00028 sec.$^{-1}$ for the end-points of 0.50 and 1.39 Mev respectively. The soft component of the spectrum falls on the curve for permitted transitions, while the hard component falls between the two curves.

Acknowledgments

The actinium preparation used in these experiments was the gift of Dr. A. v. Grosse of the University of Chicago. The writer wishes to record his sincere thanks to Dr. v. Grosse for the actinium and his careful purification of it, and to Prof. J. A. Gray for helpful advice and the privilege of carrying out some of the experiments in his laboratory. One of the preparations of uranium X was extracted by Mr. A. G. Ward and one by Dr. H. M. Cave. The writer is indebted to them, and also to Mr. J. S. Marshall and Dr. N. Feather of the Cavendish Laboratory for the third preparation of uranium X.

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THE ELECTROLYSIS OF SOME ORGANIC COMPOUNDS WITH ALTERNATING CURRENT[1]

BY J. W. SHIPLEY[2] AND M. T. ROGERS[3]

Abstract

The a-c. electrolysis of a number of organic compounds was carried out in order to ascertain what products might be obtained, what electrolytic conditions affected the nature and the yield of products, and to discover the general relations governing oxidation and reduction when a.c. is used. Oxidation was found to predominate over reduction, owing, probably, to the relatively low hydrogen overvoltage on the electrodes. The effect of varying the conditions of a-c. electrolysis was in general similar to that observed in d-c. electrolysis. Satisfactory yields were obtained only when a product of an irreversible process was concerned. A good yield of quinhydrone from the a-c. electrolysis of hydroquinone was secured at a relatively high current density. The chlorination of acetone by the a-c. electrolysis of a solution of acetic anhydride in hydrochloric acid gave a current yield of 35% at a current density of 2 amp. per cm^2.

Introduction

The alternating current electrolysis of water has been extensively studied by Shipley and Goodeve (15, 17, p. 3), and a theory developed which satisfactorily accounts for the decomposition of water into its elements. They showed that current density was the important factor in the electrolysis and that there exists a critical current density, specific for the electrode, below which no hydrogen or oxygen was evolved and above which these gases were given off in accordance with Faraday's law. The specific current density at which gases were evolved was shown to be a function of the capacity of the electrodes for storing hydrogen and oxygen.

The possibility of obtaining oxidation or reduction of organic compounds using a.c. was first shown by Drechsel (5, 6), who obtained a variety of products in small yield from the electrolysis of various organic compounds. Pearce and Couchet (13), using a.c., observed the reduction of nitrobenzene to aniline and found that high current densities were most favourable for reduction. Brochet and Petit (3, 4) found that non-reversible effects occurred on electrolyzing solutions of the salts of fatty acids, whereas Baur (1) observed that the products of a-c. electrolysis were frequently the same as those found for d-c. electrolysis but that the proportions differed. Leblanc and Schick (10, 11), from the results obtained by varying the frequency of alternation,

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calculated the duration of existence of organic radicals. Above a certain rate of alternation no product was observed. Fichter (8) found that in general, with an organic depolarizer, no compounds could be isolated using a.c. that are not obtainable with d.c. The only case observed and reported where a.c. gives a product not obtainable with d.c. is the solution of copper and other metals in potassium cyanide solutions (3, 4). The ions are removed as complexes when formed and, on the reversal of the current, the metals do not plate out.

No quantitative data relating to the electrolysis of organic compounds by a.c. could be found in the literature, and few investigations of this subject have been reported in recent years. The present work was undertaken in an attempt to determine the general relations governing oxidation and reduction, to determine the behaviour of various types of organic compounds on electrolysis, and to find reactions suitable for quantitative study using a-c. electrolysis.

It was understood that, since oxidation and reduction alternated with each change of phase of the current, only the products of irreversible processes could be expected. Relatively insoluble, non-ionizing, complex and gaseous products might however be formed and be readily separated from the electrolyte and thus have a quantitative significance. Electrode material, electrolyte temperature, voltage, frequency, and current density are conditions that affect electrolysis. The effect of varying these conditions is recorded in the experimental work but, of course, relatively few of the possible combinations could be studied.

Little is known concerning the mechanism of electrolysis and the energy distribution between electrode and electrolyte when electron exchange takes place. An accumulation of facts in regard to a-c. electrolysis should be of some value in a study of this mechanism.

Experimental

The most efficient d-c. method modified for a-c. electrolysis was chosen, but much higher current densities and in most cases platinum electrodes were used. Other electrodes, with the exception of gold and carbon, are too severely corroded by electrolysis to be of general use. Platinum itself is somewhat attacked in almost all cases. The electrodes, of 1 sq. cm. area and covered at both ends with glass, consisted of two parallel wires, an arrangement providing uniform current density. Gold electrodes were provided by plating platinum wires, whereas silver and nickel wires and zinc sticks were used for electrodes of these metals. Graphite electrodes were cut from large electrodes. The electrode vessel was a glass tube of 150 cc. capacity immersed in an ice bath and provided with a motor stirrer. Gases off the electrodes were analyzed as follows:— carbon dioxide, oxygen, and unsaturated hydrocarbons by absorption in potassium hydroxide, pyrogallol, and fuming sulphuric acid, respectively; hydrogen and carbon monoxide by combustion over

copper oxide at 300° C.; and saturated hydrocarbons by combustion with oxygen over mercury. After electrolysis the solutions were tested for the presence of primary alcohols, aldehydes, formic acid, and esters by standard qualitative methods.

A.c. taken from the 60 cycle, 110 volt circuit was regulated by resistances, and effective current voltages were measured with a-c. instruments checked against standards.

Fatty Acids and Their Salts

The a-c. electrolysis of the aliphatic acids and their salts gave products quite similar to those obtained by d-c. electrolysis. Oxidation predominates over reduction where both are possible. This is probably due to the low hydrogen overvoltages possible when a.c. is used. The ratio of ethane evolution to hydrogen evolution [ethane efficiency (9, p. 281)] was used as a measure of the relative oxidation-reduction processes when the conditions of electrolysis were varied. The solvent was water.

TABLE I

A-C. ELECTROLYSIS OF 5% POTASSIUM ACETATE. PLATINUM ELECTRODES. INFLUENCE OF CURRENT DENSITY ON ETHANE EFFICIENCY

Current density, amp. per cm².	1.0	3.0	5.0	7.0
Ethane efficiency, %	17.0	40.7	56.6	62.0
Oxygen in gas evolved, %	1.2	0.0	1.0	2.0

Increase in current density increases the ethane efficiency but changes the amount of oxygen evolved very little. Apparently the Kolbe synthesis (9, p. 279) is favoured by increase of current density, as is found to be the case in d-c. electrolysis.

TABLE II

A-C. ELECTROLYSIS OF POTASSIUM ACETATE. PLATINUM ELECTRODES. INFLUENCE OF CONCENTRATION (CURRENT DENSITY, 7 AMP. PER CM².)

Concentration, in gm. per 100 cc. water	50.0	7.5	0.75
Ethane efficiency, %	62.0	42.4	0.0
Oxygen in gas evolved, %	2.0	1.4	20.0

Increase in concentration gives a higher yield of ethane, and less oxygen is evolved, as in d-c. electrolysis. An increase in temperature was also found to lower the ethane efficiency and increase the production of oxygen. This also occurs in the d-c. electrolysis.

Varying the concentration of potassium acetate did not affect the ethane efficiency of the electrolysis appreciably, but in a neutral solution the efficiency dropped. Thus at a current density of 4 amp. per cm^2. it was found to be but 16% instead of about 48%.

Nickel and silver electrodes favoured the production of hydrogen; no ethane was detected. Carbon electrodes produced mostly hydrogen and carbon dioxide, with a little ethane, and there was disintegration of the electrodes. Iron and zinc electrodes evolved hydrogen only and the electrodes disintegrated. These results indicate that with nickel, iron, and zinc electrodes no appreciable oxidation occurs.

The addition of potassium carbonate and potassium bicarbonate to the acetate electrolyte inhibited the production of ethane. Methanol in appreciable amount was detected in the electrolyte, hence it is probable that the Hofer-Moest reaction (9, p. 285) replaces the Kolbe synthesis.

A saturated solution of potassium acetate in anhydrous acetic acid, when electrolyzed with a.c. at platinum electrodes and at a current density of 0.6 amp. per cm^2., gave an ethane efficiency of 40%. Ethane was also evolved at mercury electrodes but with lower efficiency.

Electrolysis of Potassium Propionate

A 30% solution of potassium propionate containing 2% of propionic acid was electrolyzed with a.c., and the results shown in Table III were obtained.

TABLE III

ELECTROLYSIS OF POTASSIUM PROPIONATE

Electrodes	Amp. per $cm.^2$	Per cent CO_2	Per cent O_2	Per cent H_2	Per cent hydrocarbons	
					Unsat'd	Sat'd
Platinum	0.5	30.0	4.2	53.8	5.6	6.2
Platinum	1.5	31.5	3.5	47.6	12.5	2.8
Platinum	2.7	35.1	1.2	43.4	17.9	3.6
Platinum (alkaline sol'n)	3.0	4.7	6.6	68.0	19.2	1.2
Carbon (acetic sol'n)	1.2	36.3	1.0	36.0	19.6	3.8

The oxidation increases somewhat with current density (percentage of carbon dioxide rises), and the amount of ethylene produced also increases with the current density, whereas the production of butane and oxygen decreases. The reactions concerned are probably:

$$2\ C_2H_5COO^- + H_2O_2 \longrightarrow C_4H_{10} + 2\ CO_2 + 2\ OH^-$$
$$2\ C_2H_5COO^- + H_2O_2 \longrightarrow C_2H_4 + C_2H_5COOH + CO_2 + 2\ OH^-$$
$$2\ C_2H_5COO^- + H_2O_2 \longrightarrow C_2H_5COOC_2H_5 + CO_2 + 2\ OH^-$$

the second reaction, producing ethylene, being favoured by increase of current density. The products are similar to those found in d-c. electrolysis (9, p. 300).

A-c. Electrolysis of Potassium Butyrate and Potassium n-Caproate

A saturated solution of potassium butyrate, slightly acid with butyric acid, on a-c. electrolysis using platinum electrodes and a current density of 1 amp. per cm². gave the following products:

Per cent CO_2	Per cent O_2	Per cent CO	Per cent H_2	Per cent hydrocarbons	
				Unsat'd	Sat'd
28.7	1.3	0.6	57.6	8.9	0.8

A relatively large amount of primary alcohol remained in the electrolyte, together with some esters and a trace of aldehydes. The isopropyl alcohol probably arose from the hydrolysis of propylene and the hexane by a reaction similar to that producing butane in the electrolysis of potassium propionate.

A saturated solution of *n*-potassium caproate electrolyzed with platinum electrodes at a current density of 3 amp. per cm². gave a relatively large yield of esters and alcohols, with about a 5% current efficiency yield of decane.

The Kolbe synthesis seems to occur with a-c. electrolysis of the paraffin series just as it does with d.c.

A-c. Electrolysis of Ethyl Alcohol and n-Propyl Alcohol

A solution containing 50 gm. of ethyl alcohol, 3 gm. of sulphuric acid, and 150 cc. of water was electrolyzed, platinum gauze electrodes and a current density of 3 amp. per cm². being used; temperature, 40° to 50° C. A current yield of 2.5% acetaldehyde and 8.0% acetic acid was obtained. It was hoped that a-c. electrolysis might give a higher yield of aldehyde than d.c., but this was not the case. The a-c. electrolysis of *n*-propyl alcohol gave a current yield of 17% propionic acid.

Aromatic Hydrocarbons

A 10% suspension of benzene in 100 cc. of 4% sodium sulphate was electrolyzed at 20°, with platinum gauze electrodes, at a current density of 2 amp. per cm². and with stirring. A current yield of about 1% hydroquinone was obtained. Maleic and formic acids were found, as well as other breakdown products, but most of the current is lost by the production of hydrogen and oxygen. Benzene, being insoluble in the electrolyte, is a very inefficient depolarizer. D-c. electrolysis of benzene produces quinone but with a.c. the quinone is reduced to hydroquinone on successive alternations of the current.

An emulsion of *p*-xylene in 10% sulphuric acid containing acetone (to dissolve it) was electrolyzed in a manner similar to that used for benzene but at a current density of 20 amp. per cm². The products sought were *p*-tolualdehyde and *p*-toluic acid. It was thought that the intensity of oxidation might be moderated to favour the accumulation of aldehyde, but a current

yield of only 5% aldehyde and about 1% *p*-toluic acid was obtained. Fichter (8) found 26% aldehyde and 6.4% acid as the current yield for d-c. electrolysis.

Aniline

The a-c. electrolysis of aniline in hydrochloric acid solution gave a fair current yield of aniline black. Oxidation rather than chlorination took place, since no chlorination product was detected.

Hydroquinone

A 6% solution of hydroquinone in water, to which was added a little sulphuric acid, was electrolyzed at platinum electrodes, a current density of 3 amp. per cm^2. being used. A current yield of 50% of green-black, crystalline, almost pure, quinhydrone was obtained. This a-c. electrolysis was studied in detail in order to find the operating conditions for obtaining maximum yield. A following paper records the results.

Thiourea

A-c. electrolysis of thiourea, 3 gm. in 100 cc. of 6 *N* hydrochloric acid, at current density of 2 amp. per cm^2., temperature 20° C., and treatment of the products of electrolysis with a saturated potassium nitrate solution at 0° C., gave a 13% current efficiency for oxidation, the product being $C_2H_6N_4S_2 \cdot 2HNO_3$ (dithio formamidine dinitrate). The use of sulphuric acid in place of hydrochloric acid and treatment of the electrolyte with ethyl alcohol gave a 15% current yield of $C_2H_6N_4S_2 \cdot H_2SO_4$. The polymerized oxidation product in neither case is reduced readily at platinum electrodes, nor is it very susceptible to further oxidation. The above yields are lower than those obtained in d-c. electrolysis.

Polymerization of Thiosulphate

A 20% solution of sodium thiosulphate was electrolyzed with platinum electrodes, and a series of determinations were made over a range of current densities. The sodium thiosulphate oxidized was determined by titration with iodine solution before and after the electrolysis. At a current density of 2 amp. per cm^2. the current efficiency for oxidation to S_4O_6 was 57%, but on increasing the current density above this value the yield progressively fell off. This result was not expected, but it may be explained by assuming that at high current densities hydrogen peroxide is formed in high concentration and much of it decomposes to give oxygen before S_2O_3 can diffuse in to react with it. There is also probably a high local heating effect at the electrode at higher current densities which will favour the decomposition of hydrogen peroxide and the evolution of oxygen.

Oxidation of Oxalate

The a-c. electrolysis of a saturated solution of sodium oxalate containing 5% sulphuric acid gave a marked increase in the production of carbon dioxide as the current density increased. The efficiency of the oxidation at a current

density of 2 amp. per cm^2. was 9.34%; at 3 amp. per cm^2., 17.6%; and at 6 amp. per cm^2., 29.4%.

Electrolysis of Acetone

Fifty grams of acetone in 200 cc. of 5% sulphuric acid was electrolyzed at platinum gauze electrodes with a current density of 1.0 amp. per cm^2. After passage of 30 amp.-hr. no pinacol could be detected in the electrolyte, but such oxidation products as formic and acetic acids were identified. An analysis of the gases evolved indicated that a complex electrolytic process had occurred in which oxidation had predominated.

Ammonium Thiocyanate

The a-c. electrolysis of ammonium thiocyanate was carried out, by an adaptation of the d-c. process described by Perkin (14), using 15 gm. of ammonium thiocyanate in 200 cc. of water and 20 cc. of concentrated hydrochloric acid as electrolyte, platinum electrodes, and a current density of 2 amp. per cm^2. Canarine, being insoluble, separated out but in a current yield of about one-third that obtained by d-c. electrolysis.

Potassium Ethyl Malonate

A concentrated solution of potassium ethyl malonate was prepared by saponifying diethyl malonate with the calculated amount of potassium hydroxide in ethyl alcohol. The solution was electrolyzed by a.c. in an apparatus similar to that used for acetates. No diethyl succinate could be isolated. This negative result was expected since the product is stable towards reduction and, if formed, would not be reduced.

Substitutions

(A) Chlorination of Acetone

Acetone (130 cc.) dissolved in 100 cc. of concentrated hydrochloric acid and kept below 35° C. was electrolyzed by a.c. at platinum gauze electrodes, without stirring, and a current density of 2.0 amp. per cm^2. A yellow oil separated, and after the passage of 35 amp.-hr. this oil was collected and fractionated. A 35% current yield of monochloroacetone was obtained. A variety of other chlorination products also resulted but no oxygen was evolved. The platinum electrodes dissolved slowly.

(B) Iodoform from Ethyl Alcohol

The preparation of iodoform by the method of Muller (12) was attempted by the use of a-c. electrolysis, but the results were not encouraging. The current efficiency at a current density of 2 amp. per cm^2. was only 5%.

(C) Iodination of Thymol

The method used was an adaptation of that described in a patent by Bayer and Co. (7). Thymol in 200 cc. of water containing 7 gm. of potassium iodide and 1 gm. of sodium hydroxide was electrolyzed at platinum electrodes with a current density of 1.5 amp. per cm^2. Because the product, di-thymol di-iodide, is insoluble, it was hoped that a.c. would give a satisfactory yield,

but a current yield of only about 1% was obtained. Apparently the oxidation of thymol occurred as indicated by the evolution of carbon dioxide.

Other Reactions Studied

(A) o-Nitrobenzoic Acid

Shipley and Calhoun (16) obtained a 92% yield of anthranilic acid on the reduction of *o*-nitrobenzoic acid by d-c. electrolysis. Using a.c. and platinum electrodes in an alcoholic solution containing sulphuric acid, the authors obtained only tars and resins, and no amines could be detected. Apparently at current densities between 2 to 3 amp. per cm^2. the oxidation is too intense for the production of amines.

(B) Reduction of Pyridine to Piperidine

Since piperidine is not readily oxidized to pyridine it seemed probable that this reduction might be obtained with a.c. Both platinum and zinc electrodes were used but only traces of piperidine could be found after the passage of 20 amp.-hr. The gases evolved contained 3% of carbon dioxide and 17.5% of oxygen; this indicated some complete oxidation.

(C) Reduction of Nitrates

The a-c. electrolytic reduction of potassium nitrate to potassium nitrite, using zinc and iron electrodes, mechanical stirring, and an ice cooled electrolyte, gave good results. The following data show the variation of the efficiency of reduction with current density, using zinc electrodes.

Current density, amp. per cm^2.	0.5	1.0	5.0	6.0
Reduction efficiency, %	16.4	18.4	38.8	44.0

(D) Reduction of Ethyl Benzoate

No ethyl tolyl ether was obtained in the attempted a-c. reduction of ethyl benzoate, using platinum and mercury electrodes. Mercury is an unsuitable electrode material because of its rapid corrosion and the production of salts of mercury.

Discussion

The nature of the products from the electrolysis of organic compounds with a sine wave a.c. has been determined for a number of typical compounds. Electrodes of platinum, gold, and carbon were found to be the most satisfactory. Nickel may be used in alkaline solution. Electrodes of the baser metals are unsuitable, as they are severely corroded and the products interfere with the electrolysis.

Oxidation was found to predominate over reduction where both were possible. With noble metal electrodes this might be expected, as they have relatively low hydrogen overvoltages, and a.c. will further tend to reduce the amount of reduction by preventing the hydrogen overvoltage from building

up to a value high enough to bring about reduction of the organic compound.

Bowden and Rideal (2) showed that a finite time is required for either the oxygen or hydrogen overvoltage to rise to its full value, when the current is reversed. In many cases this time was less than the total wave for a 60 cycle current; thus both reduction and oxidation would be moderated because the overvoltage of hydrogen and oxygen would be lower than the maximum during most or all of the half-wave. A high hydrogen overvoltage is usually required for efficient reduction, so the absence in all cases of any appreciable reduction with a.c. was to be expected (nitrate to nitrite in 44% yield at zinc electrodes, current density 6 amp. per cm^2., was the greatest yield obtained).

In the case of oxidation the problem in d-c. electrolysis is usually to moderate the oxidation and prevent it resulting entirely in the production of carbon dioxide and water. An a.c. might therefore be expected to be as efficient as d.c., and in certain reactions, even superior. Only in the case of oxidation of hydroquinone to quinhydrone at high current densities was this observed.

Most halogen substitution reactions consist of two separate processes—the discharge of the halogen ion and the substitution of a hydrogen atom of the organic compound by the halogen.

When the electrode is anode, an a.c. discharges the halogen ion, and, provided that the organic depolarizer can remove it sufficiently rapidly so that none is left to again take on an electron on the reversal of the current, the efficiency of a substitution reaction should be relatively high. This was found to be the case when a 35% current yield of chloroacetone was obtained in the a-c. electrolysis of acetone in concentrated hydrochloric acid.

As both oxidation and reduction occur at an electrode, the oxidation or substitution product must not be readily susceptible to reduction, or appreciable amounts would be unable to accumulate. Thus iodoform, which is rather easily reduced at a platinum cathode, gave a current yield of about 5%. Similarly a reduction product would have to be stable to oxidation to be present in good yield. This is rarely the case.

A method to prevent the oxidation of the reduced molecule is to use base metal electrodes. The hydrogen overvoltage is relatively high, so reduction is favoured, and, when the electrode becomes anode, the solution of the metal as a cation occurs rather than the alternative process—the oxidation of the compound. This was utilized in the reduction of nitrates to nitrites at zinc electrodes.

Relatively stable oxidation products, such as quinhydrone or dithioformamidine, or gases as in the case of ethane, ethylene, carbon dioxide, or insoluble compounds as in the case of aniline black, (a solid) and $C_{10}H_{22}$ (liquid). were isolated in appreciable yields by a-c. electrolysis.

Soluble compounds with soluble oxidation and reduction products, as in the case of ethyl alcohol and *p*-nitrobenzoic acids, gave mixtures of compounds all unpromising in yield as far as a method of their preparation was

concerned. The yields with a.c. were in all cases but one (that of hydroquinone) less than with d.c. There are several reasons for this. Irreversible losses of current occur owing to the capacity of the electrodes for storing electrolytic products. Reversal of the electrolytic action of one wave will occur when alternation of the current takes place. Also there is a portion of the time in which the potential of the electrodes is below the decomposition potential of the electrolyte, as the e.m.f. passes through zero twice in each wave. This portion will be negligible at high potentials but is appreciable when the potential is low.

Only for a very few reactions is it to be expected that a.c. will be of use in favouring a desired product or in increasing yield over that given by d-c. electrolysis. At high current densities, however, it will usually maintain and often increase yields, thus enabling high current densities to be efficiently used. This is illustrated above in the a-c. electrolysis of potassium acetate.

The effect of various factors on the yield of products by a-c. electrolysis depends on the nature of the reaction. Usually these factors are the same for d.c. and a.c. Thus, for the oxidation of acetates, the effect of various factors may be explained on the basis of the hydrogen peroxide theory of Glasstone and Hickling (9, p. 251). The results found by the present authors indicate that increase of current density increases ethane efficiency. As a higher concentration of hydrogen peroxide would follow increase of current density, more rapid oxidation of the acetate ion would be expected. The rate of increase in yield falls off at high current density, since acetate ions do not diffuse in rapidly enough to react with the oxygen formed from the decomposition of hydrogen peroxide. Increase of acetate concentration increases the efficiency of ethane production because acetate ions are supplied in greater concentration for the reaction with hydrogen peroxide. The presence, in large concentration, of ions foreign to the reaction, as in the experiment in which potassium bicarbonate and potassium carbonate were added, causes a lowering of the relative concentration of acetate ion, and methanol formation replaces ethane formation [the Hofer-Moest reaction (9, page 285 *et seq.*)]. Higher temperatures lower the ethane efficiency and increase oxygen evolution since hydrogen peroxide is more unstable at high temperatures. Electrodes which are good catalysts for peroxide decomposition also lower the yield. Platinum gave the highest yield of ethane, carbon much less, and nickel, lead, zinc, and iron gave none.

An indeterminate effect no doubt influencing electrolysis is that of a high local heating on the surface of the electrode. This will be almost independent of the temperature of the electrolyte, and arises in part from the recombination of products at the electrode surface. It is not unlikely that the presence of methane in the products of the electrolysis of potassium acetate in anhydrous acetic acid results from the pyrolysis of ethane on the electrode surface. The effect of this local heating on the electrolysis has not been determined.

The control of a reaction is often possible in d-c. electrolysis by careful preparation of the electrode surface. This is not practicable in a-c. electrolysis, as all forms of the same electrode material acquire the same surface a short time after the electrolysis begins.

A low current density usually is most efficient with d.c. since the oxygen or hydrogen is in low concentration over the surface of the electrode, and the depolarizer can be provided in sufficient concentration to react rapidly enough to prevent the evolution of oxygen or hydrogen, as the case may be. The existence of a capacity for electrolytic products on the electrodes necessitates, in nearly all cases, a relatively high current density (usually greater than 0.3 amp. per cm^2.) in order to obtain any net oxidation and reduction. Hence high current densities are desirable. For reactions of the type of the oxidation of acetate, in which a high concentration of active oxygen or hydrogen peroxide at the electrode raises the efficiency of oxidation, higher current densities increase the yield. This increase is limited only by the concentration of depolarizer, the rate of diffusion, and the ease with which the depolarizer is oxidized. The oxidation of $S_2O_3^=$ to $S_4O_6^=$ was found to decrease with increase of current density, probably owing to the above conditions not being fulfilled.

Recombination of evolved gases was observed in nearly all cases in which platinum electrodes were used. This recombination took place not only in the gas above the electrolyte but also in the electrolyte itself. The latter was indicated by an elevation of the current density at which evolution took place.

This recombination was assumed to be due to the catalytic action of platinum black.

An examination of the experimental results shows that a-c. electrolysis proceeds, in general, so far as the final products are concerned, in a manner similar to d-c. electrolysis, but that oxidation is favoured over reduction. Only a few of the reactions studied indicated that a-c. electrolysis might be expected to give yields comparable to d-c. electrolysis. These are the oxidation of hydroquinone to quinhydrone, the production of ethane by the electrolysis of potassium acetate in aqueous and in acetic acid solution, the chlorination of acetone, and the polymerization of thiosulphate to tetrathionate. Two of these reactions have been studied in detail and the results will appear in a following paper.

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NOTE ON THE MOUNTING OF SMALL METAL SPECIMENS IN RESIN PLAQUES

In the preparation of very small specimens of metal for polishing, etching, and metallographic examination, it was found that they could be mounted conveniently by embedding in discs of a thermoplastic synthetic resin. Samples weighing only 1 or 2 mg. were mounted in this way.

The resin was a commercial polystyrene of melting point 175 to 185° C. Its transparency is an advantage in this work. A small electrically heated screw press and a positive cylindrical mold were used. The granular resin was first molded into a disc 1 in. in diameter and ½ in. thick, a pressure of 1000 lb. per sq. in. at a temperature of 125° C. being applied.

The specimen was placed centrally on the disc and both were returned to the mold. The plunger of the mold was placed on the specimen and heat and pressure were applied as before. The resulting piece contained the metal sample firmly embedded and flush with the surface.

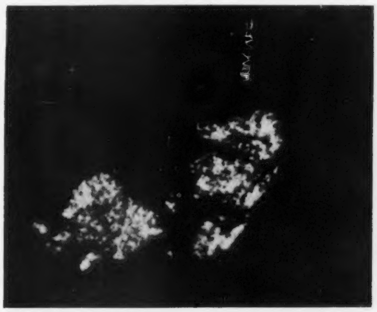

FIG. 1. *Metal flakes.* × *250.*

A photomicrograph of a mounted specimen, after polishing and etching, is shown in Fig. 1.

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THE NITRATION OF *m*-DICHLOROAZOXYBENZENE AND THE REDUCTION OF SOME OF THE PRODUCTS[1]

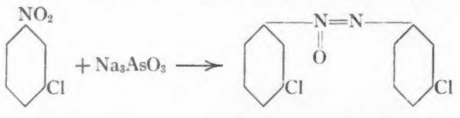
By H. E. Bigelow[2] and W. H. Steeves[3]

Abstract

The nitration of *m*-dichloroazoxybenzene and the fractional crystallization of the nitrated products is described. Evidence for the structural formula of each is given. The reduction of some of the nitro derivatives with sodium arsenite to form azobisazoxy and trisazoxy compounds containing chlorine is also discussed.

Introduction

The usual method of nitrating azoxy compounds is by treatment with concentrated or fuming nitric acid according to the number of nitro groups desired. This method was used in nitrating *m*-dichloroazoxybenzene which was prepared by reducing *m*-nitrochlorobenzene with sodium arsenite in an alkaline solution of sodium hydroxide, a new method for its preparation.



After refluxing the *m*-dichloroazoxybenzene with concentrated nitric acid, a reddish oily substance was obtained. Steam distillation of this product gave a pale yellow oil having a boiling point ranging from 75° to 235° C. No further investigation has yet been made of this oil. The solid residue, however, was subjected to a long series of fractional crystallization from which five compounds were obtained: *(A)* m.p. 116°; *(B)* m.p. 145°; *(C)* m.p. 112°; *(D)* m.p. 105°; *(E)* m.p. 157° C. All were yellow needles of different shades varying from a greenish yellow to an orange yellow. All except *(E)* were found, on analysis, to be mononitro derivatives of *m*-dichloroazoxybenzene, *(E)* being a dinitro derivative.

The determination of the structure of these compounds rests upon the established fact that substitution in the ring adjacent to the oxygen atom attached to the nitrogen of the azoxy group by a semi-polar double bond never occurs (1, p. 128). The assumption is therefore made that all substitution takes place in the one ring. To determine their structural configuration these substitution products, where possible, were reduced to the corresponding amines with scission of the azoxy-linkage. Where the amines had already been prepared the structure followed at once. In most cases, unfortunately, the amines have not yet been prepared.

[1] *Manuscript received January 9, 1939.*
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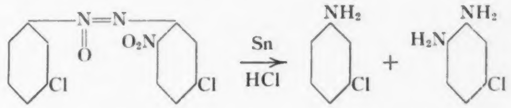
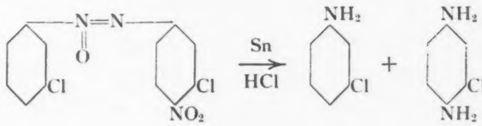
Reduction of these compounds to their corresponding amines showed that *(A)* was *o*-nitro-*m*-dichloroazoxybenzene, and *(B)* was *p*-nitro-*m*-dichloroazoxybenzene. Neither sodium amalgam nor tin and hydrochloric acid could reduce *(C)* to the corresponding amine. Instead, a white flaky compound, m.p. 169° C., resembling a hydrazo compound was obtained. However, since it has been impossible to nitrate more than one benzene ring of azoxy compounds, this is probably the other ortho derivative rather than meta, as it was found in fairly large quantity. *(D)* was found in very small quantity. Consequently no structural investigation of it has yet been made. It is, however, probably the meta derivative which would be formed in small quantity.

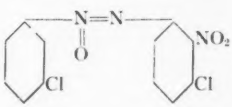
(A) m.p. 116°



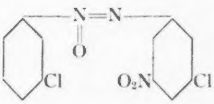
(B) m.p. 145°



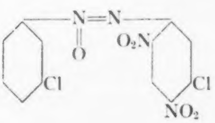
(C) m.p. 112°



(D) m.p. 105°



(E) m.p. 157°

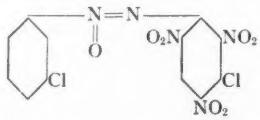


(E) was the only dinitro derivative found. Since the ortho and para positions of *m*-dichloroazoxybenzene are occupied most readily by nitro groups as indicated by the fact that, of the mononitro derivatives, *(A)* and *(B)* were found in larger quantities, the above structural formula is probably correct.

Nitration with Fuming Nitric Acid

When *m*-dichloroazoxybenzene was refluxed with fuming nitric acid two trinitro derivatives were obtained, *(F)* m.p. 182° C. and *(G)* 165° C. One

would expect the compound found in larger quantity *(G)* to be symmetrical and have the formula

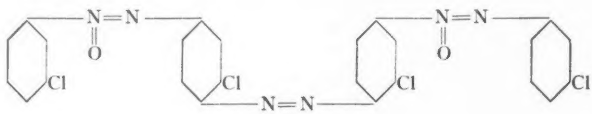


because the nitro groups would substitute ortho and para to the groups already present, and meta to one another. Further evidence for this structure for *(G)* lies in the fact that *(G)* was obtained by treating either *(A)* or *(B)* with fuming nitric acid. Thus far it has been impossible to determine with certainty the structure of these two trinitro derivatives of *m*-dichloroazoxybenzene, since they are not acted on by reducing agents such as tin and hydrochloric acid under ordinary conditions. These compounds, if reduced to aryl amines, would give amines which, as yet, have not been prepared. In consequence they have not been further studied.

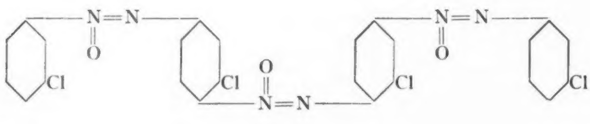
Sodium Arsenite Reduction of Nitro Derivatives

Reduction of *p*-nitro-*m*-dichloroazoxybenzene *(B)* with sodium arsenite gave *(H)* the azobisazoxy and *(I)* the trisazoxy derivatives of *m*-dichloroazoxybenzene.

(H)



(I)



The tetrachloroazobisazoxybenzene *(H)*, m.p. 210° C., was brick red in colour, while the tetrachlorotrisazoxybenzene (*I*) was bright yellow, m.p. 195° C. The latter was obtained in small quantity.

So exceedingly stable was *(H)* that it could not be oxidized to the azoxy derivative *(I)* by 90% hydrogen peroxide in glacial acetic acid. It is interesting to note that azobisazoxybenzene is oxidized by peracetic acid with ease to trisazoxybenzene (5, p. 122).

The sodium arsenite reduction of *o*-nitro-*m*-dichloroazoxybenzene *(A)* gave a gelatinous compound *(J)* which was crystallized from water. It exploded before melting at 275° C., contained no chlorine, formed a hydrochloride, m.p. 178° C., and was extremely explosive. The structure of this compound has not yet been determined.

Experimental

Preparation of m-Dichloroazoxybenzene

A paste of arsenic trioxide (76 gm.) and water was poured with continuous stirring into a solution of 100 gm. of sodium hydroxide. To this solution was added 72 gm. *m*-chloronitrobenzene. The mixture, in a two litre, three-necked, round bottom flask with 250 cc. water, was stirred for six hours at 104° C. An amount of water was then added sufficient to prevent sodium arsenate from precipitating on cooling. Dark yellow crystals of *m*-dichloroazoxybenzene, which separated on cooling, were filtered, dried, and crystallized from alcohol; m.p., 97° C. Yield, 85%.

Nitration of m-Dichloroazoxybenzene

To *m*-dichloroazoxybenzene (56 gm.) was added 250 gm. of concentrated nitric acid (sp. gr. 1.45) and the mixture refluxed for six hours. The dark red viscous oil obtained was steam distilled. The distillate contained a small amount of pale yellow oil which was found to have a boiling point ranging from 75° to 235° C.

Experience showed that one of the compounds in the residue after steam distillation was quite insoluble in cold benzene, the others were very soluble, and that this fact made possible the isolation of *(A)* for further purification. Accordingly the residue after steam distillation was crystallized from benzene by cooling with ice, filtered, and further purified by crystallizing from benzene until the melting point of the pale yellow crystals became constant at 116° C. Calcd. for *(A)* $C_{12}H_7O_3N_3Cl_2$: Cl, 22.73%; M.W., 312. Found: Cl, 22.58%; M.W., 310.

Separation by Fractional Crystallization

The mother liquor from *(A)* was evaporated on a steam bath and the residue was subjected to a long series of fractional crystallization from an equal mixture of benzene and alcohol. Four compounds were obtained having constant melting points in the following order: *(B)* 145°; *(C)* 112°; *(D)* 105°; and *(E)* 157° C. All of these compounds crystallized in yellow needles of different shades, and all except *(E)* were found on analysis to be mononitro derivatives of *m*-dichloroazoxybenzene. *(E)* was found to be a dinitro derivative. *(A)* and *(B)* were obtained in fairly large quantities, about 20% each, *(C)* about 4%, and *(D)* and *(E)* in very small quantities—less than 1%. Calcd. for *(B)* $C_{12}H_7O_3N_3Cl_2$: Cl, 22.73%. Found: Cl, 22.46%. Calcd. for *(C)* $C_{12}H_7O_3N_3Cl_2$: Cl, 22.73%. Found: Cl, 22.70%. Calcd. for *(D)* $C_{12}H_7O_3N_3Cl_2$: C, 46.15; H, 2.46; Cl, 22.73%; M.W., 312. Found: C, 46.16; H, 2.83; Cl, 22.48%; M.W., 313.7. Calcd. for *(E)* $C_{12}H_6O_5N_4Cl_2$: N, 15.69%; Found: N, 15.75%.

Reduction of (A), m.p. 116° C., with Tin and Hydrochloric Acid

The reduction of this compound took place with difficulty forming tarry materials and yielding only a very small quantity of the corresponding amines.

Five grams *(A)* was reduced with tin and hydrochloric acid at room temperature over a period of seven days. The resulting mixture was made basic, extracted with ether, and crystallized from benzene and ligroin. *m*-Chloraniline was obtained along with a small amount of yellow crystals, m.p. 73 to 76° C., that of 4-chloro-1,2-diaminobenzene (3, p. 555; 4, p. 773). This established the structure of *(A)*.

Reduction of (B), m.p. 145° C., with Tin and Hydrochloric Acid

In the presence of alcohol and water *(B)* was reduced with tin and hydrochloric acid. After heating on a steam bath for two hours, the mixture was poured into an excess of 20% sodium hydroxide. The base was extracted with ether, evaporated, and crystallized from benzene and ligroin. *m*-Chloraniline was obtained along with yellow crystals having constant m.p. 63° C., that of 2-chloro-1,4-diaminobenzene (2). Evidently compound of m.p. 145° C. was *p*-nitro-*m*-dichloroazoxybenzene.

Reduction of Compound (C), m.p. 112° C., with Tin and Hydrochloric Acid

This compound, as has already been stated, gave a white flaky material having m.p. 169° C. when reduced with tin and hydrochloric acid. On analysis this product showed that the reduction was incomplete and suggested some type of hydrazo derivative. Other reducing agents were used but so far it has been impossible to reduce the compound to the amine.

Nitration with Fuming Nitric Acid

m-Dichloroazoxybenzene (50 gm.) was refluxed for two hours with 200 gm. of fuming nitric acid. The resulting mass was poured into water and neutralized with sodium bicarbonate. The solid yellow product was subjected to a series of fractional crystallizations from an equal mixture of alcohol and benzene. Two trinitro derivatives were obtained, *(G)* m.p. 165° C. and *(F)* m.p. 182° C. *(G)* appeared first and was obtained in larger quantity. When crystallizations were made from benzene alone, *(F)* appeared first. *(G)* was also obtained by nitrating either of the mononitro derivatives *(A)* or *(B)*. Calcd. for *(F)*, trinitro derivative, $C_{12}H_5O_7N_5Cl_2$: C, 35.8; H, 1.24; Cl, 17.6%; M.W., 402. Found: C, 36.8; H, 1.25; Cl, 17.2%; M.W., 400.9. Calcd. for *(G)*, trinitro derivative, $C_{12}H_5O_7N_5Cl_2$: Cl, 17.62%; M.W., 402. Found: Cl, 17.69%; M.W., 401.

Preparation of Azobisazoxy and Trisazoxy Derivatives

The reduction of *p*-nitro-*m*-dichloroazoxybenzene (*B*) with sodium arsenite was brought about by adding 6 gm. of *(B)* to a solution of 15 gm. of arsenic trioxide, 20 gm. of sodium hydroxide in 100 gm. of water, and 25 gm. of alcohol. The mixture was refluxed and stirred with a mechanical stirrer in a three necked flask for two hours. A reaction took place causing the mixture to turn a deep red suggesting an azo compound. Before cooling, 300 gm. of water was added to keep the sodium arsenate in solution. After cooling, the mixture was filtered, dried, and crystallized from benzene. The brick

coloured mass was recrystallized from benzene until the melting point became constant at 210° C. This, on analysis, was shown to be *m*-tetrachloroazobisazoxybenzene. Calcd. for $C_{24}H_{14}O_2N_6Cl_4$: Cl, 25.36%. Found: Cl, 25.33%.

From the crude benzene mother liquors of the azobisazoxy derivatives was isolated a small quantity of pale yellow crystals having m.p. 195° C. A micro analysis of this compound showed it to be *m*-tetrachlorotrisazoxybenzene. Calcd. for $C_{24}H_{14}O_3N_6Cl_4$: N, 14.58%. Found: N, 14.33%.

Reduction of o-Nitro-m-dichloroazoxybenzene (m.p. 116° C.)

The sodium arsenite reduction of this compound did not take place in the usual manner. Neither an azobisazoxy nor a trisazoxy compound was formed. Instead a water soluble product was obtained which was extremely explosive on heating and which formed a well defined hydrochloride with m.p. 178° C. It is hoped that in the near future the structure of this highly explosive compound will be determined.

Acknowledgment

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